



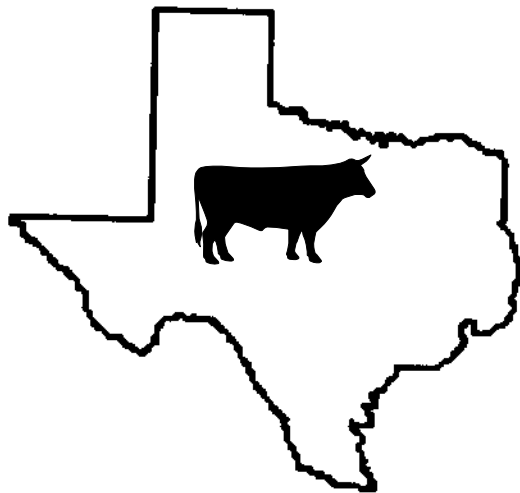
**U.S. Fish and Wildlife Service  
Region 2  
Contaminants Program**



**PHASE II CONTAMINANTS INVESTIGATION  
OF BUFFALO LAKE NATIONAL  
WILDLIFE REFUGE, TEXAS  
1993 - 1994**

by

Denise L. Baker <sup>1</sup>, Joel D. Lusk <sup>2</sup>, and Craig M. Giggelman



U.S. Fish and Wildlife Service  
Arlington Ecological Services Field Office  
711 Stadium Drive, East, Suite #252  
Arlington, Texas 76011

September 1998

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**ABSTRACT**

Buffalo Lake National Wildlife Refuge is located in the Southern High Plains in Randall County, Texas. The lake from which the Refuge received its name has not contained water since the 1980s. In 1987, a Phase I contaminants investigation of the Refuge was conducted by the U.S. Fish and Wildlife Service, Arlington, Texas, Field Office. The results of this investigation indicated that elevated concentrations of nutrients (nitrogen and phosphorus compounds), salts, copper, strontium, and zinc were found in and downstream of cattle feedlot waste retention lagoons; Tierra Blanca Creek, the major lotic contributor of the Refuge, had degraded water quality, primarily attributed to run-off and discharges from cattle feedlots; and that nutrient concentrations retained in soils in the dry reservoir bed in Buffalo Lake National Wildlife Refuge were elevated to the extent that inundation could create unacceptably high nutrient concentrations in the surface water. Consequentially, in 1993, a Phase II contaminants study was initiated at the Refuge by the U.S. Fish and Wildlife Service to evaluate the extent of contamination in stormwater run-off entering the Refuge via Tierra Blanca Creek; to determine the extent of contamination in soils and vegetation within the Refuge; to evaluate the ability of crops grown in the Refuge to reduce soil contaminant concentrations; and to monitor contaminant levels in soils, surface water, and vegetation of moist soil management units constructed in the southern portion of the Refuge. To accomplish these objectives, surface water samples, representing a stormwater surge, were collected in Tierra Blanca Creek, upstream of the Refuge, analyzed for nutrient and total metal content, and compared with water data from the Phase I study and criteria values protective of aquatic life. Surface water, groundwater, soil, and biological samples were collected within the boundaries of the Refuge and analyzed for total metal and nutrient content. Data from these water analyses were compared with criteria and other screening values protective of aquatic life, while data obtained from the soils component of this study were compared with U.S. median background levels. The soil data were also statistically compared with data from the Phase I study to determine if contaminant levels had increased or decreased within the Refuge between 1987 and 1993. Biological samples consisting of vegetation and terrestrial invertebrates were analyzed for total metals. The resulting data from this portion of the study were statistically analyzed and compared with criteria protective of wildlife to determine the bioavailability of contaminants within the Refuge. In 1994, sediment and additional surface water, groundwater, soil, and biological samples were collected from the Refuge. The water samples were analyzed for dissolved metal and nutrient content. Soil and sediment samples were analyzed for total metal and nutrient content. Biological samples consisted of vegetation, aquatic macroinvertebrates, aquatic vertebrates, and avian specimens which were analyzed for total metals. In addition, sediment, soil, and biological samples were analyzed for total polychlorinated biphenyls and organochlorine pesticide residues. Water, soils, sediment, and biological data resulting from these analyses were compared with criteria and screening values protective of wildlife resources to further interpret contaminant levels within the Refuge.

In general, surface water in Tierra Blanca Creek appeared to be as contaminated in 1993 as it was in 1987. This may be attributed to residual nitrates and other nutrient compounds leaching from sediments which were previously saturated with contaminants because the rainfall event sampled was not of significant duration or intensity to cause the discharge of nutrient laden waste from cattle feedlots located upstream of the Refuge. With the exception of one pond (Pond No. 2), surface water within the Refuge was relatively un-impacted by contaminants. Pond No. 2 contained elevated metals which

may be attributed to the high clay content within the sediments. No obvious trends of contaminant infiltration into the groundwater at the Refuge were detected.

Farming of selected areas within the dry reservoir bed at the Refuge has been practiced since 1988. Detected phosphorus levels in soils from this area were lower in 1993 in comparison to the soils data collected in 1987; however, nitrogen soil levels were elevated in comparison to the 1987 data. Significant surface water inflow into the Refuge has not occurred since the Phase I study was conducted in 1987. Nutrient contaminants in run-off from the cattle feedlots that stimulated undesirable eutrophic conditions and caused fish kills in the reservoir now appear to function as fertilizer for crops in the dry reservoir bed. The nitrogen levels in the soils were elevated but did not appear to be causing adverse effects to wildlife that feed on plants grown in these soils. Metal concentrations detected in soils of the dry reservoir bed were not at levels considered detrimental to wildlife. Nitrogen levels detected in soils from the moist soil management units were more elevated than concentrations detected in the dry reservoir bed. This may be attributed to the moist soil management units functioning in the capacity of wetlands, thus acting as sinks for nutrients transported into the Refuge via Tierra Blanca Creek. Total polychlorinated biphenyls and residual organochlorine pesticides did not appear to represent a concern within the Refuge.

Based on the results of this study, vegetation and wildlife currently at the Refuge do not appear to be adversely impacted. As long as the dry reservoir bed within the Refuge is managed as a grassland, and not as a reservoir, there is no cause for concern. However, if the reservoir is allowed to fill again, eutrophication will likely occur resulting in situations similar to the 1960s and 1970s fish kills. The moist soil management units located in the southern portion of the Refuge serve as a limited buffer against contaminated stormwater intrusion from Tierra Blanca Creek. However, it is suggested that regulatory agencies re-evaluate permitting so many large scale cattle feedlots in such a small watershed that contains sensitive habitats, because the potential exists that Buffalo Lake National Wildlife Refuge could be severely impacted by millions of gallons of raw, untreated waste from these feedlots in the event of a rainfall of significant intensity and duration.

**Project ID No. 9320001-2N14**

<sup>1</sup>Denise L. Baker is the Supervisory Environmental Contaminants Specialist with the U.S. Fish and Wildlife Service Region 1 Field Office, 510 Desmond Drive SE, Suite 102, Lacey, Washington 98503-1273.

<sup>2</sup>Joel D. Lusk is an Environmental Specialist with the U.S. Fish and Wildlife Service Region 2 Field Office, 2105 Osuna NE, Albuquerque, New Mexico 87113.

Acknowledgments: The authors wish to express their extreme gratitude to Mr. Lynn Nymeyer and Ms. Kathy Payne for their tireless efforts in monitoring rainfall and collecting samples. The authors also wish to acknowledge Mr. Alvin Payne for preparing the sampling vehicle and expediting the safety training. The authors wish to further acknowledge Ms. Joy Winkel for assistance in preparation of the study proposal and work plan.

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**TABLE OF CONTENTS**

INTRODUCTION . . . . .	1
STUDY AREA & BACKGROUND . . . . .	1
MATERIALS & METHODS . . . . .	5
RESULTS & DISCUSSION . . . . .	10
CONCLUSIONS & RECOMMENDATIONS . . . . .	31
REFERENCES . . . . .	33
LIST OF FIGURES & TABLES . . . . .	ii

## LIST OF FIGURES & TABLES

Figure 1.	Buffalo Lake National Wildlife Refuge . . . . .	2
Figure 2.	Tierra Blanca Creek Watershed . . . . .	3
Figure 3.	Tierra Blanca Creek Sampling Sites . . . . .	6
Figure 4.	Sampling Sites within Buffalo Lake National Wildlife Refuge . . . . .	7
Figure 5.	Organic Nitrogen in Tierra Blanca Creek, 1987 & 1993 . . . . .	14
Figure 6.	Total Kjeldahl Nitrogen in Tierra Blanca Creek, 1987 & 1993 . . . . .	14
Figure 7.	Total Nitrate-Nitrogen in Tierra Blanca Creek, 1987 & 1993 . . . . .	15
Figure 8.	Ammonia-Nitrogen in Tierra Blanca Creek, 1987 & 1993 . . . . .	15
Figure 9.	Chemical Oxygen Demand in Tierra Blanca Creek, 1987 & 1993 . . . . .	16
Table 1.	Comparison of 1993 Tierra Blanca Creek Water Quality Data with Surface Water Quality Criteria for Texas Streams and Other Numeric Criteria . . . . .	10
Table 2.	Comparison of 1993 Water Quality Data from Buffalo Lake National Wildlife Refuge Surface Water Impoundments with Surface Water Quality Criteria for Texas Streams and Other Numeric Criteria . . . . .	11
Table 3.	Intercept and Slope Values for Determining Dissolved Metals Concentrations from Total Metals Concentrations in Water . . . . .	12
Table 4.	Mean Nutrient and Metals Concentrations in Surface Water Collected from the Four Ponds at Buffalo Lake National Wildlife Refuge, in 1994 . . . . .	17
Table 5.	Mean Nutrient and Metals Concentrations in Groundwater Collected from Buffalo Lake National Wildlife Refuge, in 1993 and 1994 . . . . .	18
Table 6.	Mean Nutrient and Metals Concentrations in Sediments Collected from the Four Ponds at Buffalo Lake National Wildlife Refuge, in 1994 . . . . .	19
Table 7.	Comparison of Metals Concentrations of Soils Collected in Buffalo Lake National Wildlife Refuge in 1993 with Background Concentrations in Soils of the United States . . . . .	21
Table 8.	Results of ANOVA and Tukey's HSD Test of Means from the Comparison Between the Three 1993 Soil Cropping Treatments and the 1987 Soils Data at Buffalo Lake National Wildlife Refuge . . . . .	22
Table 9.	Mean Nutrient and Metals Concentrations in Soils Collected from the Five Moist Soil Management Units, Buffalo Lake National Wildlife Refuge, in 1994 . . . . .	23

Table 10.	Comparison of Metals Concentrations in Plant Tissues Collected from Buffalo Lake National Wildlife Refuge in 1993 with Diagnostic Concentrations Considered Protective of Wildlife . . . . .	25
Table 11.	Results of ANOVA and Tukey's HSD Test of Means of Plants Collected from Three Cropping Treatments at Buffalo Lake National Wildlife Refuge, in 1993 . . . . .	26
Table 12.	Mean Concentrations of Metals and Organochlorines Detected in Biological Samples Collected from Stewart Marsh and the Five Moist Soil Management Units at Buffalo Lake National Wildlife Refuge, in 1994 . . . . .	27
Table 13.	Mean Metals Concentrations in Composite Biological Samples Collected from the Four Ponds at Buffalo Lake National Wildlife Refuge, in 1994 . . . . .	28
Table 14.	Comparison of Metals Concentrations in Grasshoppers Collected from Buffalo Lake National Wildlife Refuge in 1993 with Diagnostic Concentrations Considered Protective of Wildlife . . . . .	29
Table 15.	Results of ANOVA and Tukey's HSD Test of Means of Grasshoppers Collected from Two Cropping Treatments at Buffalo Lake National Wildlife Refuge, in 1993 . . . .	30
Table 16.	Metals Concentrations Detected in Avian Species Collected at Buffalo Lake National Wildlife Refuge, in 1994 . . . . .	31

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**INTRODUCTION**

In 1987, a Phase I contaminants investigation of Buffalo Lake National Wildlife Refuge was conducted by the U.S. Fish and Wildlife Service (USFWS), Arlington, Texas, Field Office. The results of this investigation indicated that elevated concentrations of nutrients (nitrogen and phosphorus compounds), salts, copper, strontium, and zinc were found in and downstream of cattle feedlot waste retention lagoons; Tierra Blanca Creek, the major lotic contributor of the Refuge, had degraded water quality, primarily attributed to run-off and discharges from cattle feedlots; and nutrient concentrations retained in soils in the dry reservoir bed in the Refuge were elevated to the extent that inundation could create unacceptably high nutrient concentrations in the surface water (Irwin and Dodson, 1991). Consequentially, in 1993, a Phase II contaminants study was initiated at the Refuge by the USFWS to evaluate the extent of contamination in stormwater run-off entering the Refuge via Tierra Blanca Creek; to determine the extent of contamination in soils and vegetation within the Refuge; to evaluate the ability of crops grown in the Refuge to reduce soil contaminant concentrations; and to monitor contaminant levels in soils, surface water, and vegetation of moist soil management units constructed in the southern portion of the Refuge. To accomplish these objectives, surface water samples, representing a stormwater surge, were collected in 1993 from Tierra Blanca Creek upstream of the Refuge, analyzed for nutrient and total metal content, and compared with water data from the Phase I study and criteria protective of aquatic life. Surface water, groundwater, soil, and biological samples were collected within the boundaries of the Refuge in 1993 and analyzed for total metal and nutrient content. The resulting data from the water analyses were compared with criteria and other screening values protective of aquatic life. Data obtained from the soils component of this study were compared with U.S. median background levels to interpret the extent of contamination within the Refuge. Soil data were also statistically compared with data from the Phase I study to determine if contaminant levels had increased or decreased within the Refuge between 1987 and 1993. Biological samples consisting of vegetation and terrestrial invertebrates were analyzed for total metals. The resulting data were statistically analyzed and compared with criteria protective of wildlife to determine the bioavailability of contaminants within the Refuge.

In 1994, sediment and additional surface water, groundwater, soil, and biological samples were collected from the Refuge. The water samples were analyzed for dissolved metal and nutrient content. Soil and sediment samples were analyzed for total metal and nutrient content. Biological samples consisted of vegetation, aquatic macroinvertebrates, aquatic vertebrates, and avian specimens which were analyzed for total metals. Sediment, soil, and biological samples were also analyzed for total-polychlorinated biphenyls (PCBs) and organochlorine pesticide residues. Water, soils, sediment, and biological data resulting from these analyses were compared with criteria and screening values protective of wildlife resources to further interpret contaminant levels within the Refuge.

**STUDY AREA & BACKGROUND**

Buffalo Lake National Wildlife Refuge consists of 7,664 acres (3,102 hectares) and is located within the Tierra Blanca Creek watershed in the mixed to short grass prairie area of the Southern High Plains, in Randall County in the Texas Panhandle (Figure 1). The Refuge provides habitat supporting eight species of amphibians (Dixon, 1987); 34 species of reptiles including the Texas horned lizard (*Phrynosoma*

*cornutum*), a species listed as threatened by the State of Texas (Dixon, 1987); and 25 species of mammals (Davis and Schmidly, 1994). In addition, 344 avian species have been observed at the Refuge, including the bald eagle (*Haliaeetus leucocephalus*), a federally listed threatened species, the whooping crane (*Grus americana*), and the interior least tern (*Sterna antillarum*), both federally listed endangered species (U.S. Fish and Wildlife Service, 1997). The climate of the area is considered semi-arid. Temperature ranges from 21.2°F (-5.9°C) to 91.7°F (33.2°C). Winds are predominantly out of the south-southwest (National Weather Service, pers. comm., 1998). Average annual rainfall is approximately 16 inches (41 cm) (New Mexico Water Quality Control Commission, 1994). Hydrologically, the principal lotic system entering the Refuge is Tierra Blanca Creek, an intermittent tributary of Palo Duro Creek which in turn, is a tributary of the Upper Prairie Dog Town Fork of the Red River (Texas Red River Segment No. 0229) (Texas Natural Resource Conservation Commission, 1996b). Tierra Blanca Creek's watershed consists of approximately 1,724 square miles (4,465 square kilometers) and encompasses portions of Quay and Curry Counties in New Mexico, and Deaf Smith, Parmer, Castro, and Randall Counties in Texas (Figure 2). In the past, this creek was a perennial system; however, due to the reduction of surface water run-off attributed to the construction of water retention structures on farm and rangeland within the watershed, and the lowering of the groundwater table resulting from the draw down of the High Plains (Ogallala) Aquifer for water supply purposes, recharge has become negligible and, with the exception of major storm events of unusual intensity, the system no longer has continuous flow (U.S. Bureau of Reclamation, 1985).

Soil types along Tierra Blanca Creek consist of sandy loams which are shallow to moderately deep over caliche. These soils are considered part of the Ulysses - Mansker Association and the Mansker - Berda -

**Figure 1. Buffalo Lake National Wildlife Refuge.**

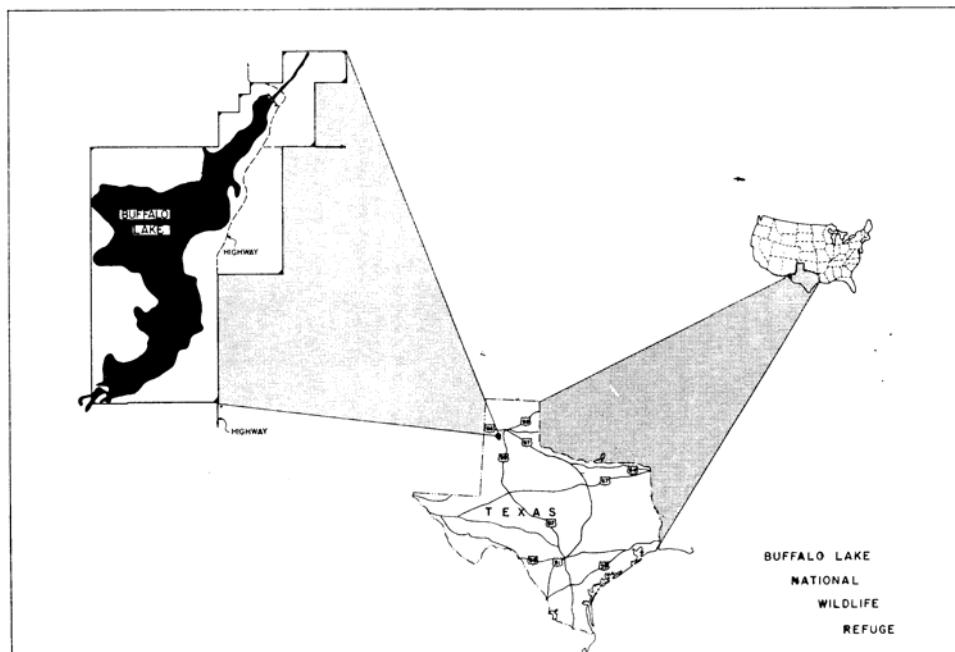
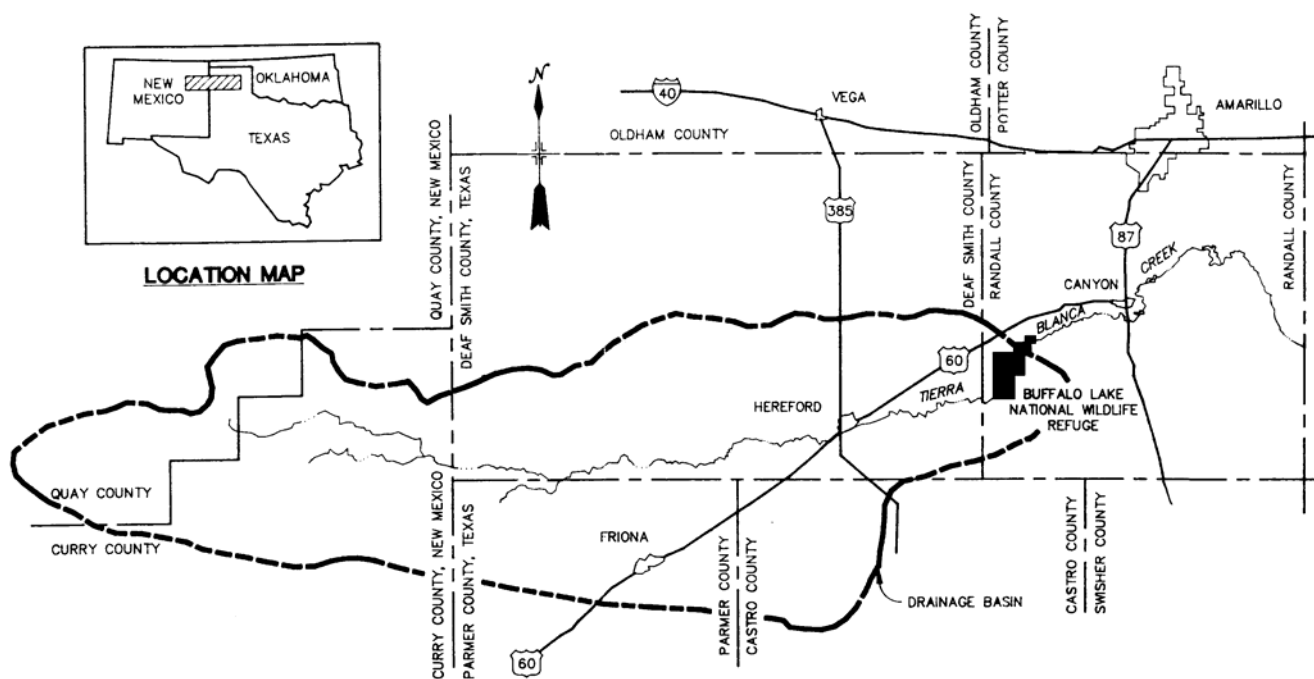


Figure 2. Tierra Blanca Creek Watershed.



Series consist of calcareous gravelly loams that also occur in upland areas. In the Refuge, the reservoir Potter Association. Both the Ulysses Series and Mansker Series contain calcareous loamy soils that occur in upland areas. Winter wheat, grain, sorghum, and native grasses are typically grown in Ulysses soils. Berda Series soils are characterized as being well drained, granular soils of upland areas. Soils in the Potter bed consists of broken Spur clay loam intermixed with Ulysses clay loam. Soils from the Spur Series are characterized as deep, well-drained, soils that developed under mid to short grasses in calcareous sediments prior to alluvial deposition (U.S. Department of Agriculture, 1970).

Geologically, the Refuge overlays the Ogallala and the Dockum Group Aquifers. The Ogallala Aquifer is composed of unconsolidated, fine to coarse grained sand, clay, and silt with interbedded cemented zones of calcium carbonate. Water pumped from this aquifer usually contains total dissolved solids (TDS) ranging from 500.0 - 1000.0 mg/l; sulfate levels < 300.0 mg/l; chloride concentrations < 300.0 mg/l; nitrate levels which can exceed the primary drinking water standard of 10.0 mg/l; and fluoride concentrations which can exceed the primary safe drinking water standard of 4.0 mg/l (Texas Water Commission, 1989). Average annual recharge is approximately 0.058 inches (0.147 cm) per year, while annual drawdown from pumpage is approximately 3.73 inches (9.47 cm) (Nativ, 1988). The Dockum Group (Santa Rosa) Aquifer underlies the Ogallala Aquifer and is composed of interbedded shale, sand, sandstone, and conglomerate strata. Water from this aquifer usually contains TDS < 1000.0 mg/l (Texas Water Commission, 1989).

An estimated 140,260 people live in the Texas Counties encompassed by the Tierra Blanca Creek watershed (Texas A&M University, 1997). The closest urban area upstream of the Refuge is the City of Hereford, which has a population of approximately 14,745 people (Texas Department of Transportation, 1994) and is located approximately 12 miles (19.32 kilometers) southwest of the Refuge. The economy of the area is based primarily on agriculture, livestock production, and limited gas and oil exploration and production.

Buffalo Lake was created as a flood control impoundment of Tierra Blanca Creek by the construction of Umbarger Dam, an earthen retention structure, in 1939. At its maximum surface water volume, the reservoir exhibited a storage capacity of 30,122 acre-feet (37,159,077 cubic meters) and a surface area of 2,828 acres (1,144.5 hectares) (U.S. Bureau of Reclamation, 1984). The reservoir's shallow wetlands in conjunction with adjacent agricultural cropland attracted millions of waterfowl migrating along the Central Flyway (U.S. Fish and Wildlife Service, 1984). This reservoir also provided a valuable source of recreation for the human populace inhabiting the local area. On November 17, 1959, to better perpetuate the migratory avian resources, the USFWS assumed trusteeship for the reservoir and established Buffalo Lake National Wildlife Refuge by Secretarial Order 2843 (GEI, 1991). In 1964, 1967, 1968, 1969, 1971, and 1973, prior to the establishment and active enforcement of regulations governing unauthorized discharges within the State of Texas, large fish kills occurred at Buffalo Lake which were attributed to run-off and discharges from cattle feedlots located in Hereford and other areas within the Tierra Blanca Creek watershed, upstream of the Refuge (U.S. Bureau of Reclamation, 1985; Texas Parks and Wildlife Department, 1997). During these events, ammonia levels as high as 22.9 mg/l were detected in surface water samples collected from the reservoir (Texas Parks and Wildlife Department, 1997). Over time, as a result of the reduction of inflow, accumulation of sediments, and excess nutrient loading, the water quality deteriorated in Buffalo Lake. The reservoir was drained in 1978 so that construction of a concrete dam, also known as Umbarger Dam, could be initiated for flood control purpose. The earthen retention structure had been deemed hydraulically inadequate to control large flood flows after inspections conducted by the U.S. Army Corps of Engineers, the U.S. Bureau of Reclamation, and the Texas Department of Water Resources (U.S. Bureau of Reclamation, 1985). Even though the concrete dam was completed in 1993, because of chronic water quality problems and inadequate inflow, the reservoir has remained dry and not functioned as a viable lentic system since it was drained (U.S. Bureau of Reclamation, 1985; Nymeyer, pers. comm., 1998). Use of the Refuge by migratory waterfowl and other aquatic avian species declined probably due to the lack of available surface water. In an attempt to re-establish use of the Refuge by migratory waterfowl, Stewart Dike, a low level earthen dike, was constructed in the southern portion of the dry reservoir bed to retain water and develop five moist soil management units in the area known as Stewart Marsh. These units have been flooded with well water from the Dockum Group Aquifer to compensate for the nutrient loading received from the periodic inflow of Tierra Blanca Creek during storm events. In addition four small,

circular ponds have been constructed in the dry reservoir bed at the Refuge to maintain water for avian species and other wildlife. The remainder of the dry reservoir bed is used for cultivating milo, sorghum, and winter wheat (Nymeyer, pers. comm., 1998).

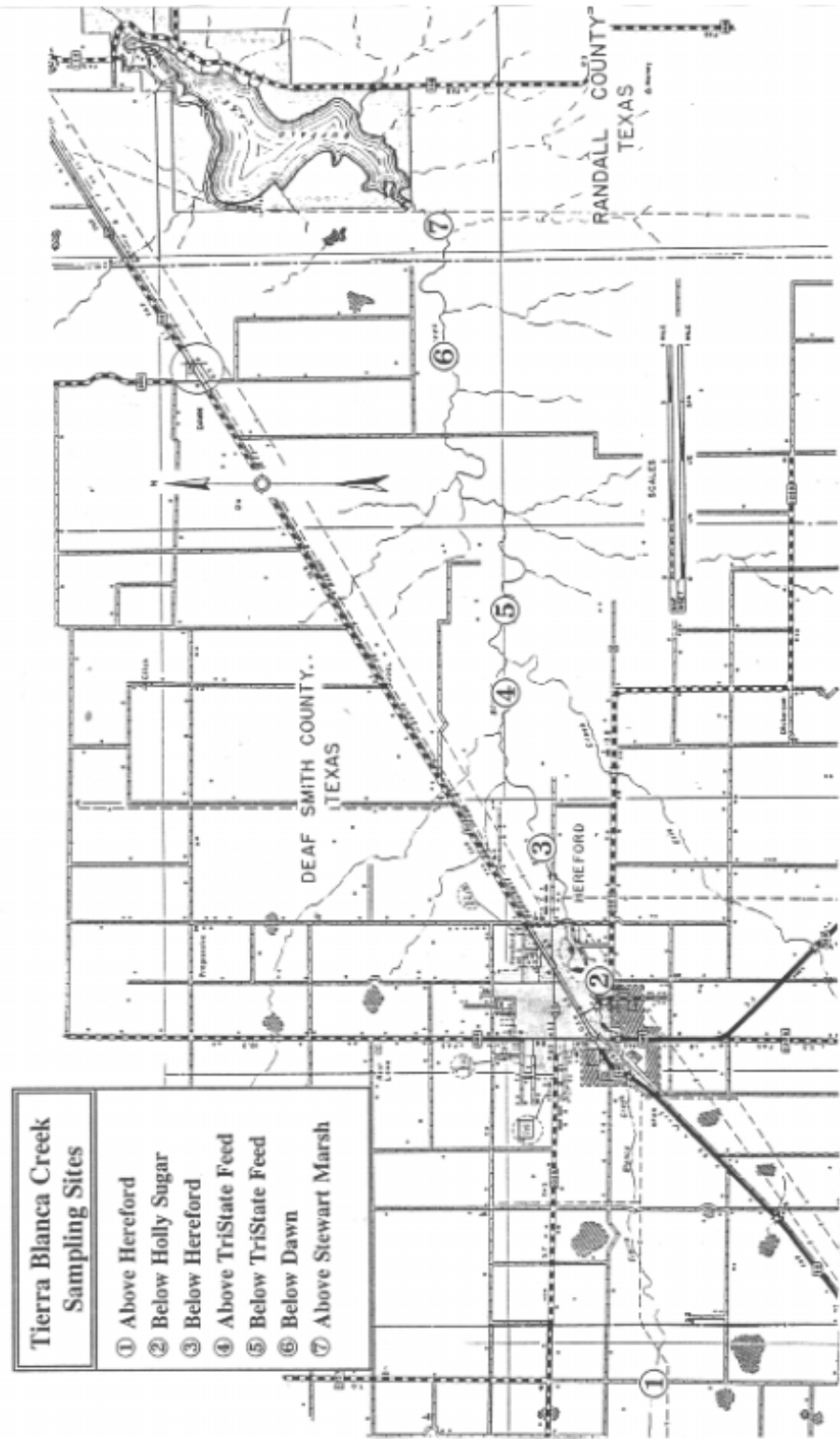
Currently, there are 18 permitted feedlots or concentrated animal feeding operation facilities (CAFOs) located within the Tierra Blanca Creek watershed upstream of the Refuge. Each one of these facilities contains over 5,000 head of cattle, and collectively these CAFOs contain over 600,000 head (Southwestern Public Service Company, 1998). In a typical CAFO, one head will produce approximately 34.0 cubic feet (0.96 cubic meters) of manure in a one year period. A CAFO encompassing 10.0 acres (4.05 hectares) that contains 1,000 head will generate the same amount of waste as a community of 6,000 people inhabiting the same acreage (U.S. Environmental Protection Agency, 1972). In accordance with *Title 30 of the Texas Administrative Code, Chapter 321, Subchapter B*, CAFOs in the State of Texas are now required to contain wastes on-site in structures such as retention lagoons and are prohibited from discharging these wastes to the Waters of the State except when experiencing rainfall greater than a 24-hour, 25-year storm event. The waste associated with the retention lagoons is usually high in nitrogen, phosphorus, trace elements, and other organic compounds which result in eutrophic conditions when discharged into a surface water body.

## METHODS & MATERIALS

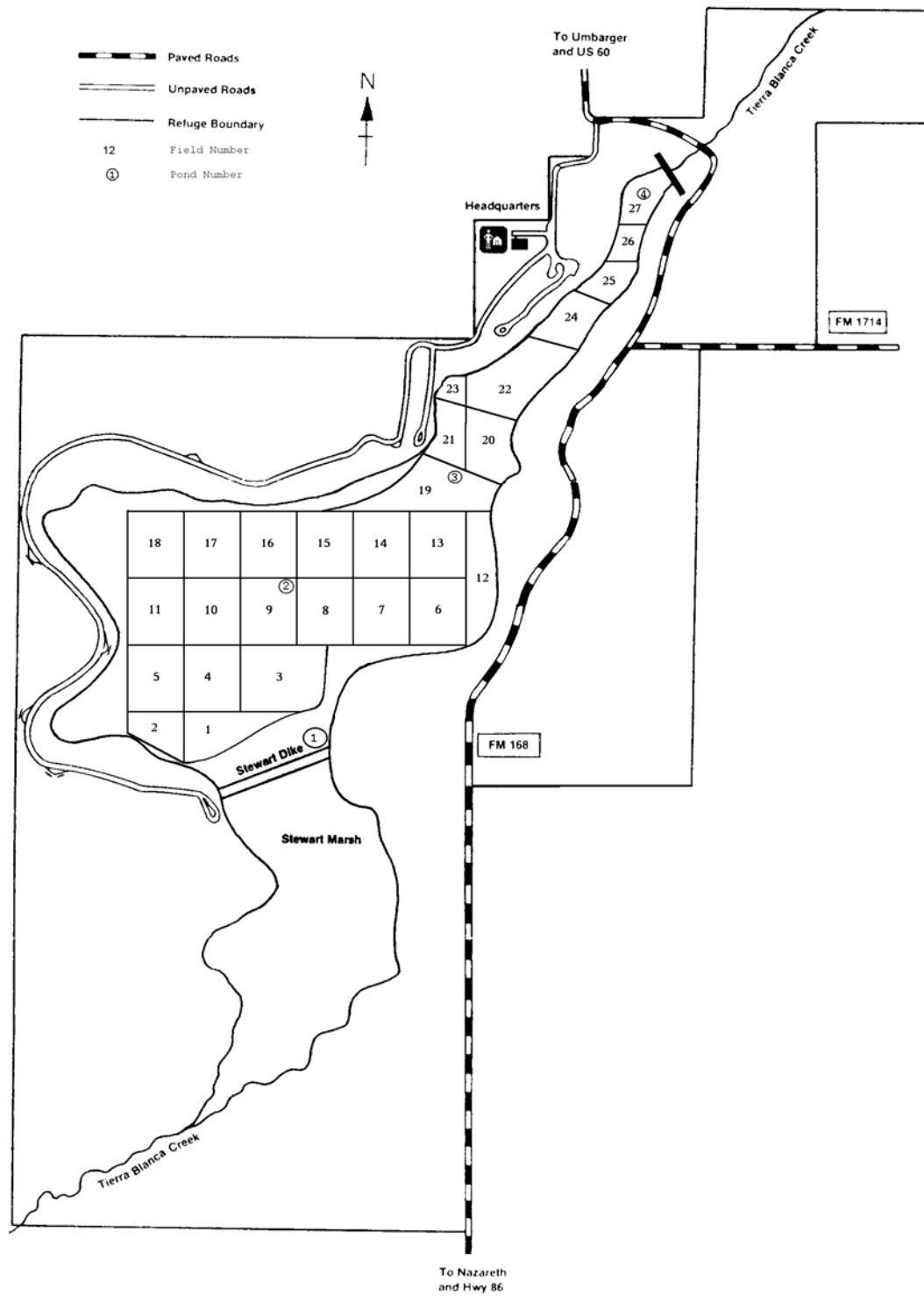
Sampling for this study was conducted by the Arlington field office staff and Refuge personnel between August 1993 and June 1994. All chemical analyses were performed at Hazleton Environmental Services, Inc., Madison, Wisconsin, contract laboratory through the USFWS Patuxent Analytical Control Facility. The Patuxent Analytical Control Facility was responsible for assessing quality assurance and control procedures for all chemical analyses conducted by the contract laboratory and assuring that these procedures were followed.

In August, 1993, surface water samples representing a stormwater surge were collected from Tierra Blanca Creek, upstream of the Refuge above and below the City of Hereford; below the Holly Sugar Plant in Hereford; above and below the TriState Feedyard outside of Hereford; below the City of Dawn; and above Stewart Marsh (Figure 3). These samples were collected by Refuge staff within a few hours after the initiation of a rain event. Additional surface water samples were collected from within the boundaries of the Refuge at Stewart Marsh and at the four ponds located in the dry reservoir bed (Figure 4). Representative groundwater samples were collected within the Refuge from the windmill cistern at Grazing Unit No. 6, located south of Stewart Dike and west of Stewart Marsh. A portion of the water samples were collected using 1.0 liter, precleaned polyethylene bottles. These samples were not filtered, but were preserved with 5.0 ml of concentrated nitric acid, frozen, and shipped refrigerated to the contract laboratory for the analyses of total aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, magnesium, manganese, mercury, molybdenum, nickel, lead, selenium, strontium, vanadium, and zinc. Simultaneously, additional water samples were collected in 1.0 liter, glass bottles and preserved with 5.0 ml concentrated sulfuric acid. These samples were shipped refrigerated for the following nutrient analyses: ammonia-nitrogen ( $\text{NH}_3\text{-N}$ ), total Kjeldahl nitrogen (TKN), organic nitrogen (O-N), nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ), and total phosphorus (TP). In addition, these samples were analyzed for total organic carbon (TOC) and chemical oxygen demand (COD). Arsenic and selenium concentrations were determined by a graphite furnace procedure. Mercury concentrations were determined by cold vapor atomic absorption. All other metallic analytes were determined by inductively coupled plasma spectroscopy. Nutrients, TOC, and COD concentrations were determined by standard methods approved

Figure 3. Tierra Blanca Creek Sampling Sites.



**Figure 4. Sampling Sites within Buffalo Lake National Wildlife Refuge.**



by the Patuxent Analytical Control Facility. The resulting water data were compared with recommended aquatic life protection criteria developed by federal, state, and other agencies. In addition, water data from Tierra Blanca Creek were compared with results from the Phase I study to determine if contaminant levels had increased or decreased within the creek between 1987 and 1993.

In June, 1994, sediment samples and additional surface water samples were collected at the Refuge from each of the four ponds. Additional groundwater samples were also collected from Grazing Unit No 6. Water samples were collected with chemically cleaned polyethylene containers, filtered through a 0.45 micron mesh filter, and preserved with 0.5 ml of nitric acid. These samples were analyzed for dissolved aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, copper, iron, magnesium, manganese, molybdenum, nickel, lead, selenium, strontium, vanadium, zinc, and total mercury content. Additional water samples were collected in the same manner, but preserved with 0.5 ml of sulfuric acid and analyzed for the same nutrient and organic constituents as previously mentioned. The data resulting from these analyses were compared with recommended criteria protective of aquatic fauna to interpret the degree of contamination present in the Refuge.

All sediment samples were collected using a hand-held, polycarbonate WildCo core sampler to a depth of 5.0 inches (13.0 cm). Sampling equipment was decontaminated after each sampling station. A portion of the sediment samples was placed in whirlpaks, frozen, and submitted for analyses of the same metals, nutrient compounds, and organic parameters as stated above. Additional sediment samples collected from Pond No. 1 and Pond No. 2 were placed in foil, frozen, and submitted for analyses of the organochlorine compounds: hexachlorobenzene (HCB), total-polychlorinated biphenyls (PCBs), alpha-benzene hexachloride ("BHC), " -chlordane, beta-benzene hexachloride (\$-BHC), dieldrin, endrin, gamma-benzene hexachloride ((-BHC), (-chlordane, heptachlor epoxide, mirex, *o,p'*-dichlorodiphenyldichloroethane (DDD), *o,p'*-dichlorodiphenyldichloroethylene (DDE), *o,p'*-dichlorodiphenyltrichloroethane (DDT), oxychlordane, *p,p'*-DDD, *p,p'*-DDE, *p,p'*-DDT, toxaphene, and trans-nonachlor. Arsenic and selenium were determined by a graphite furnace procedure. Mercury was determined by cold vapor atomic absorption. All other metallic analytes were determined by inductively coupled plasma spectroscopy while nutrient compounds were determined by standard methods approved by the Patuxent Analytical Control Facility. Organochlorine concentrations were determined by Sonication extraction. Sediment data resulting from these analyses were compared with recommended criteria protective of benthic fauna to interpret the degree of contamination present in the Refuge.

In 1993, 50 composite soil samples were collected from three cropping treatments located within the dry reservoir bed of the Refuge (Figure 4) to determine the level of contaminants retained in soils and evaluate the effectiveness of farming practices in reducing residual contaminant concentrations. Four fields per cropping treatment were randomly selected. These cropping treatments included wheat (Field Nos. 4, 7, 11, and 13), sorghum, representing a milo/sudan grass combination (Field Nos. 5, 6, 10, and 19), and fallow fields (Field Nos. 1, 12, 21, and 25). Two random transects were established across each field and a small off-road vehicle was used to access random points along the transects for collecting samples. Two composite soil samples were collected per transect. All soil samples were collected using a hand-held, polycarbonate WildCo core sampler to a depth of 3.0 inches (8.0 cm), sifted with a stainless steel and brass sieve, placed in precleaned jars, frozen, and submitted for analyses for the same metal, nutrient, and organic constituents as were the sediment samples. In 1994, soil samples were also collected from the five moist soil management units (MSMUs) located in Stewart Marsh (Figure 4). Two transects were randomly established at each of the MSMUs. Samples were randomly collected from each of the transects in the same manner as mentioned above and analyzed for the same constituents. Additional soil samples were collected from MSMU No.2 and submitted for total-PCBs and organochlorine pesticide analyses. Data from the cropping treatments were statistically analyzed using Statgraphics Plus, Version 6 for comparison to the 1987 Phase I contaminants study. The soils data were also compared to soil medians in the United States to interpret the degree of contamination present in the Refuge.

Biological samples were collected from the Refuge and consisted of terrestrial and aquatic vegetation, terrestrial and aquatic macroinvertebrates, aquatic vertebrates, and avian species. Composite terrestrial

plant samples were collected concurrently with the soil samples from the three cropping treatments at 23 sites within the dry reservoir bed to determine the extent of contamination in vegetation in the Refuge and to evaluate the ability of crops to reduce soil contaminants. Because the wheat crop had failed to grow, *Kochia* plants were collected as a substitute. Sudan grass was collected from sorghum fields and *Kochia* plants were collected from the fallow fields. Plants of uniform size were cut at the soil's surface, bagged without washing, and refrigerated until submitted for chemical analyses. Approximately 16 non-budding smartweed (*Polygonum lapathifolium*) samples, 12 to 18 inches (30.5 to 45.7 cm) tall, were collected from each of the MSMUs. These plants were cut at the soil's surface, bagged, and frozen. At the Arlington field office laboratory, prior to shipping for analyses, the plants were washed with de-ionized water (DI) and a liquinox solution, rinsed with DI water, and the leaves and leafy tops were composited without the stems. All vegetation samples were submitted for analyses of the same total metal constituents as previously mentioned. In addition to comparing the results of the analyses with criteria protective of wildlife, data from the cropping treatments vegetation were statistically analyzed using Statgraphics Plus, Version 6.

The remaining biological samples were collected to determine the concentrations of contaminants present in succeeding trophic levels. Aquatic vegetation samples were collected from Pond No. 1, Pond No. 2, and Pond No. 4. The vegetation collected included *Chara* sp., pondweed (*Potamogeton pusillus*), bulrush (*Sirpus* sp.), and sedge (*Cyperus* sp.) seeds. These samples were rinsed with water from the site, placed in plastic bags, frozen, and refrigerated until submitted for total metals analyses. Aquatic macroinvertebrate samples consisted of composite damselfly larvae (species unidentified) collected from Pond No. 1, Pond No. 3, and Pond No. 4. These samples were collected with a dip net, placed in whirlpaks, frozen, and submitted refrigerated for total metals analyses. Aquatic vertebrate samples consisted of tadpoles (species unidentified) and black bullhead catfish (*Ameiurus melas*). The composite tadpole sample was collected from Pond No. 3 with a dip net, placed in a whirlpak, frozen and submitted refrigerated for total metals analyses. Six composite black bullhead samples were collected with a cast net from Stewart Marsh after a rainfall event. These fish were non-resident organisms which had been washed down into the marsh by the storm from an unknown site, upstream of the Refuge. Four of these fish samples were placed in plastic bags and frozen until submitted for total metals analyses. The remaining two composite samples were wrapped in foil, frozen, and submitted for analyses of organochlorine pesticide residues and total-PCBs. Terrestrial macroinvertebrate samples consisted of composite grasshopper (species unidentified) samples which were collected with a dip-net from the fallow field in the vicinity of Pond No. 1, and from three of the four selected sorghum fields. Approximately 20 individuals were collected at each site, bagged, frozen, and refrigerated until submitted for total metals analyses. The avian species collected consisted of mourning doves (*Zenaidura macroura*) and red-winged blackbirds (*Agelaius phoeniceus*). A fledgling mourning dove and a fledgling red-winged blackbird were collected by hand in the vicinity of Pond No. 1. These organisms were euthanized, wrapped in plastic, frozen, and shipped refrigerated for total metals analyses. A mourning dove embryo and three red-winged blackbird eggs were also collected by hand in the same area. The mourning dove embryo was submitted for total metals and organochlorine analyses. The contents of the red-winged blackbird eggs were removed, placed in foil, and frozen until submitted for analyses of organochlorine content. In addition, an unidentified avian fledgling species was collected with a dip net already dead (cause of death unknown) from Pond No. 4. Upon collection, this organism was bagged and frozen until submitted for total metals analyses. Metals were determined in biological samples by the same procedures as previously mentioned. Organochlorine content in biological samples was determined by Soxhlet extraction. Biological data resulting from the analyses were compared with recommended predator protection limits to determine if detected contaminant concentrations represent levels of concern in succeeding trophic levels. Predator protection limits are non-enforceable, recommended guideline concentrations that are based on dietary thresholds and below which no adverse toxicological effects are observed. In addition, grasshopper data from the cropping treatments were statistically analyzed using Statgraphics Plus, Version 6.

## RESULTS & DISCUSSION

Results of the contaminants analyses in mg/l (ppm) for surface water samples representing the stormwater surge collected from Tierra Blanca Creek in 1993 are summarized in Table 1. The results for surface water samples collected from the four ponds and Stewart Marsh in 1993 are summarized in Table 2. These results were compared with federal and state recommended chronic criteria protective of aquatic life. Chronic aquatic life criteria are non-enforceable guidelines based on known chronic toxicological trends. In turn,

**Table 1. Comparison of 1993 Tierra Blanca Creek Water Quality Data with Surface Water Quality Criteria for Texas Streams and Other Numeric Criteria.** (Note: DR is ratio of number of analytical detections to number sampled; Min is minimum detected concentration; O (mean) is average detected concentration; Max is maximum detected concentration; N/A is not applicable; and < is less than)

Analyte	Tierra Blanca Creek (mg/l, total)				Criteria (mg/l, dissolved)
	DR	Min	O*	Max	
Aluminum (Al)	7/7	3.90	14.20	32.90	0.087 (a)
Arsenic (As)	6/7	0.001	0.002	0.003	0.190 (b)
Boron (B)	7/7	0.052	0.077	0.121	0.750 (c)
Barium (Ba)	7/7	0.089	0.186	0.405	no criterion
Beryllium (Be)	5/7	<0.001	0.001	0.003	0.005 (c)
Chromium (Cr)	7/7	0.005	0.011	0.023	0.318 (b)
Copper (Cu)	7/7	0.004	0.010	0.020	0.020 (b)
Iron (Fe)	7/7	2.26	7.70	16.50	1.000 (a)
Magnesium (Mg)	7/7	5.44	7.66	13.70	no criterion
Manganese (Mn)	7/7	0.051	0.288	0.939	0.100 (c)
Nickel (Ni)	7/7	0.004	0.10	0.026	0.245 (b)
Lead (Pb)	4/7	0.005	0.011	0.025	0.0062 (b)
Strontium (Sr)	7/7	0.156	0.198	0.308	no criterion
Vanadium (V)	7/7	0.016	0.043	0.100	no criterion
Zinc (Zn)	7/7	0.027	0.046	0.082	0.165 (b)
TKN	7/7	1.40	5.55	14.10	0.100 (d)
O-N	7/7	0.91	3.97	12.60	no criterion
NH <sub>3</sub> -N	7/7	0.490	1.46	1.97	1.000 (b)
NO <sub>3</sub> -N	7/7	0.160	4.29	14.30	1.000 (b)
TP	5/7	0.010	0.066	0.140	0.200 (b)
TOC	7/7	3.20	9.70	16.20	no criterion
COD	7/7	12.40	80.00	181.00	no criterion
Chlorides	7/7	1.70	6.10	13.00	37,000.00 (b)
Alkalinity	N/A	70.00	84.00	129.00	N/A
Hardness	N/A	57.00	70.00	80.00	N/A

\*Where concentrations were not detected above the analytical detection limit, the conservative approach of selecting the numeric value immediately below the detection limit was employed in calculating the mean.

(a) Texas Natural Resource Conservation Commission, 1996a.

(b) Texas Natural Resource Conservation Commission, 1996b.

(c) U.S. Environmental Protection Agency, 1986.

(d) U.S. Army Corps of Engineers, 1994.

**Table 2. Comparison of 1993 Water Quality Data from Buffalo Lake National Wildlife Refuge Surface Water Impoundments with Surface Water Quality Criteria for Texas and Other Numeric Criteria.** (Note: DR is ratio of number of analytical detections to number sampled; Min is minimum detected concentration; O (mean) is average detected concentration; Max is maximum detected concentration; N/A is not applicable; and < is less than)

Analyte	Stewart Marsh & Ponds No. 1- 4 (mg/l, total)				Criteria (mg/l, dissolved)
	DR	Min	O*	Max	
Al	5/5	0.38	21.50	86.60	0.087 (a)
As	5/5	0.003	0.014	0.038	0.190 (b)
B	5/5	0.065	0.360	1.21	0.750 (c)
Ba	5/5	0.117	0.227	0.435	no criterion
Be	2/5	<0.001	0.0013	0.003	0.005 (c)
Cr	3/5	0.001	0.014	0.055	0.318 (b)
Cu	3/5	0.001	0.010	0.034	0.020 (b)
Fe	5/5	0.231	11.80	46.80	1.000 (a)
Mg	5/5	7.40	50.90	148.00	no criterion
Mn	5/5	0.020	0.179	0.582	0.100 (c)
Ni	3/5	0.001	0.010	0.035	0.245 (b)
Pb	1/5	<0.010	0.012	0.023	0.0062 (b)
Sr	5/5	0.227	1.48	3.90	no criterion
V	5/5	0.160	0.125	0.491	no criterion
Zn	5/5	0.007	0.044	0.138	0.165 (b)
TKN	5/5	0.470	1.89	3.71	0.100 (d)
O-N	5/5	0.36	1.16	2.75	no criterion
NH <sub>3</sub> -N	5/5	0.110	0.896	1.81	1.000 (b)
NO <sub>3</sub> -N	5/5	0.390	0.684	1.02	1.000 (b)
TP	4/5	0.010	0.074	0.240	0.200 (b)
TOC	5/5	3.61	8.07	12.30	no criterion
COD	5/5	8.20	34.00	50.50	no criterion
Hardness	N/A	97.00	552.00	1,130.00	N/A

\*Where concentrations were not detected above the analytical detection limit, the conservative approach of selecting the numeric value immediately below the detection limit was employed in calculating the mean.

(a) Texas Natural Resource Conservation Commission, 1996a.

(b) Texas Natural Resource Conservation Commission, 1996b.

(c) U.S. Environmental Protection Agency, 1986.

(d) U.S. Army Corps of Engineers, 1994.

chronic toxicity refers to the effects of a contaminant to an organism or group of organisms over an extended period of time and may be expressed in terms of an observation period equal to the lifetime of an organism or to the time span of more than one generation. Chronic effects often occur in the population

rather than in the individual organism. Some toxicological effects may be reversible, but most are not (U.S. Environmental Protection Agency, 1986). With the exception of mercury, criteria developed by federal and state agencies for metals in surface water are based on dissolved concentrations. Water samples collected from Tierra Blanca Creek and the Refuge in 1993 were analyzed for total metal concentrations. In water chemistry, dissolved metals represent a component of total metals. The fraction of dissolved metals per total metal concentration can be estimated by employing the following equation:

$$\frac{C}{C_T} = \frac{1}{1 + (K_d \times TSS \times 10^{-6})}$$

where:

- C = dissolved metal concentration;
- C<sub>T</sub> = total metal concentration;
- K<sub>d</sub> = 10<sup>b</sup> x TSS<sup>m</sup> = linear partition coefficient;
- TSS = total suspended solids (mg/l);
- b = intercept;
- m = slope.

(Texas Natural Resource Conservation Commission, 1995)

TSS levels in surface water samples collected in 1993 were not analyzed; however, assuming that the TSS levels would be similar to values measured in the Phase I study, dissolved concentrations for copper, lead, and zinc in water samples collected from Tierra Blanca Creek were determined by employing a TSS value of 122.0 mg/l (from Irwin and Dodson, 1991) with the intercept and slope values presented in Table 3. The

**Table 3. Intercept and Slope Values for Determining Dissolved Metals Concentrations from Total Metals Concentrations in Water.\***

Metal	Lotic Systems		Lentic Systems	
	Intercept	Slope	Intercept	Slope
As	5.68	-0.73	5.68	-0.73
Cr	6.52	-0.93	6.34	-0.27
Cu	6.02	-0.74	6.45	-0.90
Ni	5.69	-0.57	6.34	-0.76
Pb	6.45	-0.80	6.31	-0.53
Zn	6.10	-0.70	6.52	-0.68

\*Texas Natural Resource Conservation Commission, 1995.

results indicated that the mean detected copper, lead, and zinc concentrations were below the aquatic life criteria values recommended by the State of Texas for the Prairie Dog Town Fork of the Red River (Texas Natural Resource Conservation Commission, 1996b). Cadmium (detection limit = 0.001 mg/l), mercury (detection limit = 0.0002 mg/l), molybdenum (detection limit = 0.008 mg/l), and selenium (detection limit = 0.002 mg/l) were not detected above the detection limits in any of the samples from the creek. Mean total beryllium, and boron concentrations were detected below the dissolved criteria values recommended by the U.S. Environmental Protection Agency (USEPA) for the protection of aquatic fauna and plants (U.S. Environmental Protection Agency, 1986). Mean total arsenic, chromium, and nickel, concentrations were detected below the levels protective of aquatic life recommended by the State of Texas (Texas Natural Resource Conservation Commission, 1996a and 1996b). Barium, magnesium, strontium and vanadium do not currently have designated acute or chronic aquatic life protection screening values for surface water in the State of Texas. Detected barium concentrations were below 50.0 mg/l, which according to the USEPA (1986), represents the concentration where toxicological effects to aquatic organisms would begin to be

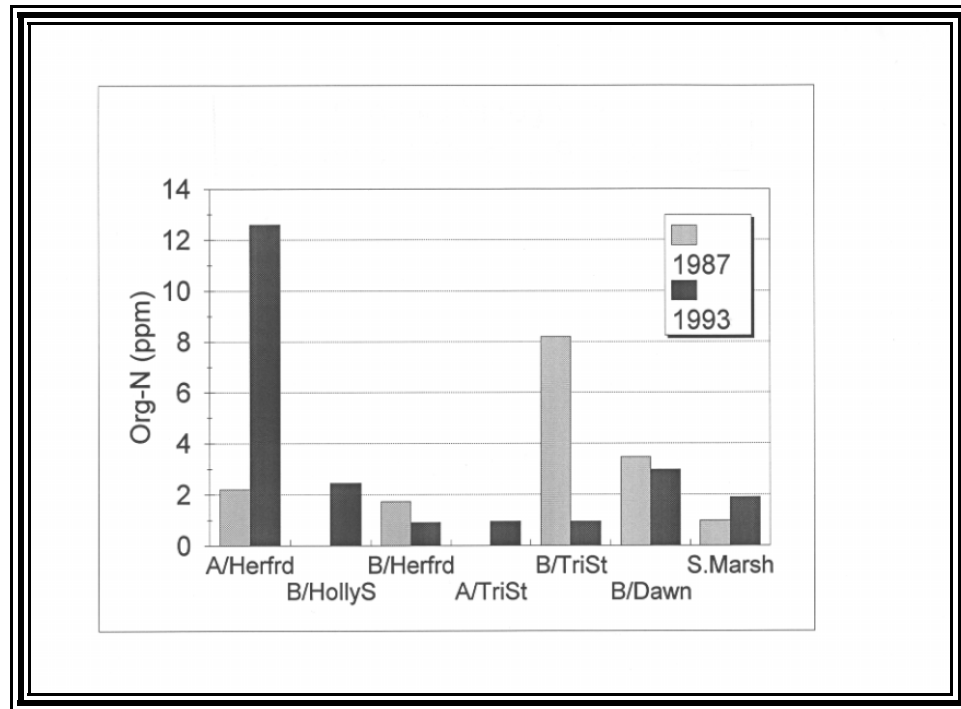
observed. Magnesium in natural waters comes mainly from the leaching of igneous and carbonate rocks. In areas where these sources are common, magnesium concentrations in water often range from 5.0 - 50.0 mg/l (Lind, 1985). Detected magnesium concentrations were below 500 mg/l which, according to Roline and Boehmke (1981), represents the concentration toxic to aquatic organisms. Detected aluminum and manganese concentrations appeared to be elevated. Both aluminum and manganese are common components of soils and sediments. The detected levels may be attributed to soil erosion and leaching within the watershed.

Total phosphorus (TP) and chlorides were below levels of concern (Texas Natural Resource Conservation Commission, 1996b). Total nitrogen (TKN), ammonia-nitrogen ( $\text{NH}_3\text{-N}$ ), and nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) levels exceeded the screening values recommended by the State of Texas (Texas Natural Resource Conservation Commission, 1996b). In unpolluted waters, ammonia compounds generally occur at 1.0 mg/l or less. Raw, untreated domestic wastewater generally contains between 12.0 - 50.0 mg/l ammonia-nitrogen. Free ammonia at levels above 2.5 mg/l is toxic to most freshwater organisms. However, low ammonia concentrations corresponding to high nitrate concentrations indicates that nitrification has occurred because raw untreated wastewater generally does not contain nitrates. (Texas Engineering Extension Service, 1989). Nitrification appears to be occurring within the stream because the detected ammonia concentrations were less than the detected nitrate concentrations. Aquatic life protection criteria or screening values have not been established by the State for organic nitrogen (O-N) in surface waters. Organic nitrogen represents nitrogen which is bound into proteins, amino acids, and urea. In untreated wastewater, 35.0 mg/l would be considered high, while 8.0 mg/l would be considered low (Qasim and Udomsinrot). Comparing the nutrient data from this study with data collected from the Phase I study indicated that organic nitrogen and total nitrogen concentrations were higher in samples collected from above the City of Hereford and above Stewart Marsh in 1993 (Figures 5 and 6); nitrate-nitrogen levels were higher in samples collected above Hereford, below TriState Feeds, below Dawn, and above Stewart Marsh in 1993 (Figure 7); and ammonia-nitrogen concentrations were higher above Hereford, below TriState Feed, and above Stewart Marsh in 1993 (Figure 8).

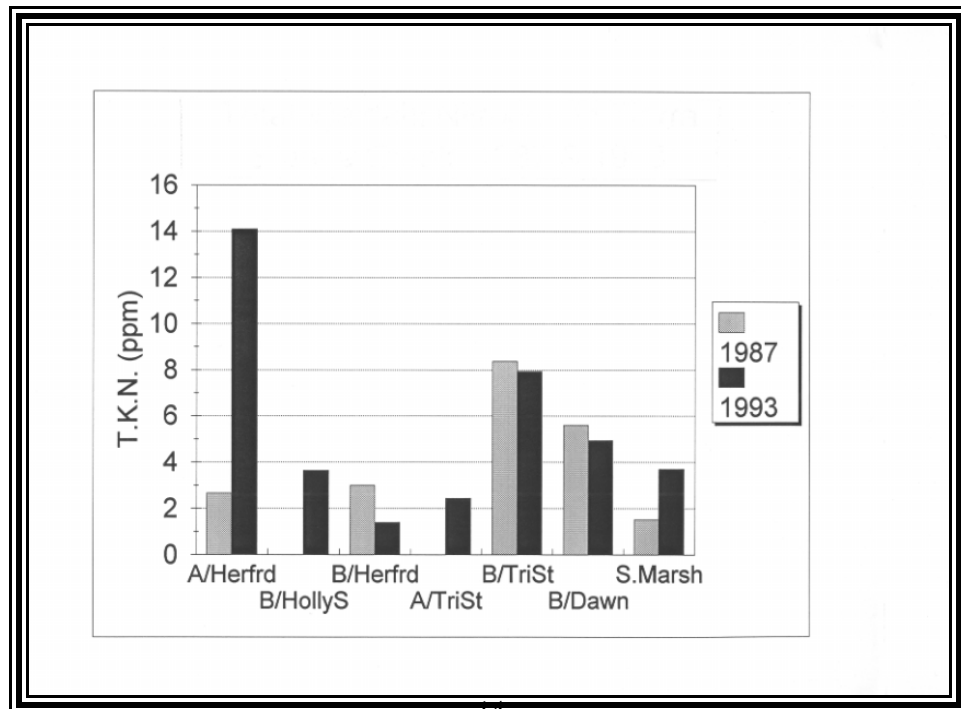
There are currently no criteria for total organic carbon (TOC) or chemical oxygen demand (COD) for surface waters in the State of Texas. In water, TOC is a measure of the amount of organic matter present. In untreated wastewater, 290.0 mg/l would be considered a high concentration while 80.0 mg/l would be considered low (Qasim and Udomsinrot). The detected TOC concentrations in samples collected from Tierra Blanca Creek in 1993 were well below 80.0 mg/l and slightly less than the values detected in the Phase I study which ranged from 10.0 - 34.5 mg/l (Irwin and Dodson, 1991). In water, COD is a measure of the amount of oxygen required to oxidize organic matter (Qasim and Udomsinrot). According to Irwin and Dodson (1991), COD concentrations in surface water in excess of 150.0 mg/l coupled with elevated biochemical oxygen demand and low dissolved oxygen concentrations could represent a cause of concern for fish and wildlife resources within the watershed. Detected values in water samples collected from the creek in 1993 were below 150.0 mg/l, except for the samples collected above the City of Hereford. Comparing COD data from this study with data collected during the Phase I study indicates that COD levels in the creek were higher above Hereford, below Dawn, and above Stewart Marsh in 1993 (Figure 9).

Water samples collected in 1993 from the surface water impoundments located within the boundaries of the Refuge contained mean concentrations of arsenic, barium, beryllium, boron, chromium, copper, lead, magnesium, nickel, and zinc concentrations below levels of concern. Cadmium (detection limit = 0.001 mg/l), mercury (detection limit = 0.0002 mg/l), and selenium (detection limit = 0.002 mg/l) were below the detection limits in all of the samples analyzed. Aluminum, iron, and manganese concentrations

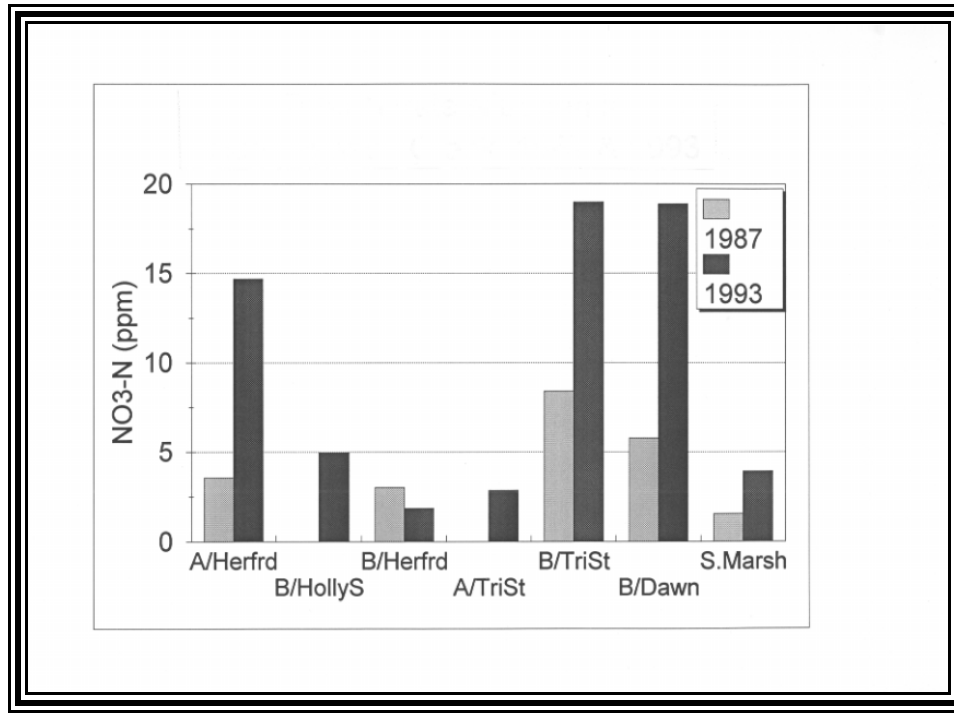
**Figure 5. Organic Nitrogen in Tierra Blanca Creek, 1987 & 1993.** (Note: A/Herfrd is above the City of Hereford; B/HollyS is below Holly Sugar Plant; B/Herfrd is below the City of Hereford; A/TriSt is above TriState Feedyard; B/TriSt is below TriState Feedyard; B/Dawn is below the City of Dawn; and S.Marsh is above Stewart Marsh)



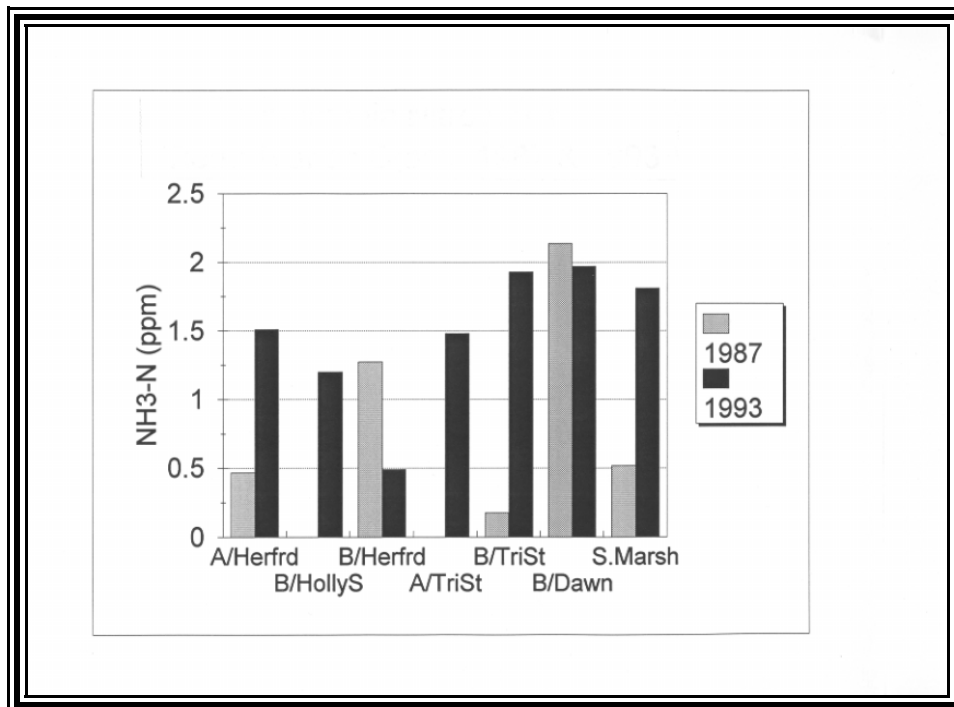
**Figure 6. Total Kjeldahl Nitrogen Concentrations in Tierra Blanca Creek, 1987 & 1993.** (Note: A/Herfrd is above the City of Hereford; B/HollyS is below Holly Sugar Plant; B/Herfrd is below the City of Hereford; A/TriSt is above TriState Feedyard; B/TriSt is below TriState Feedyard; B/Dawn is below the City of Dawn; and S.Marsh is above Stewart Marsh)



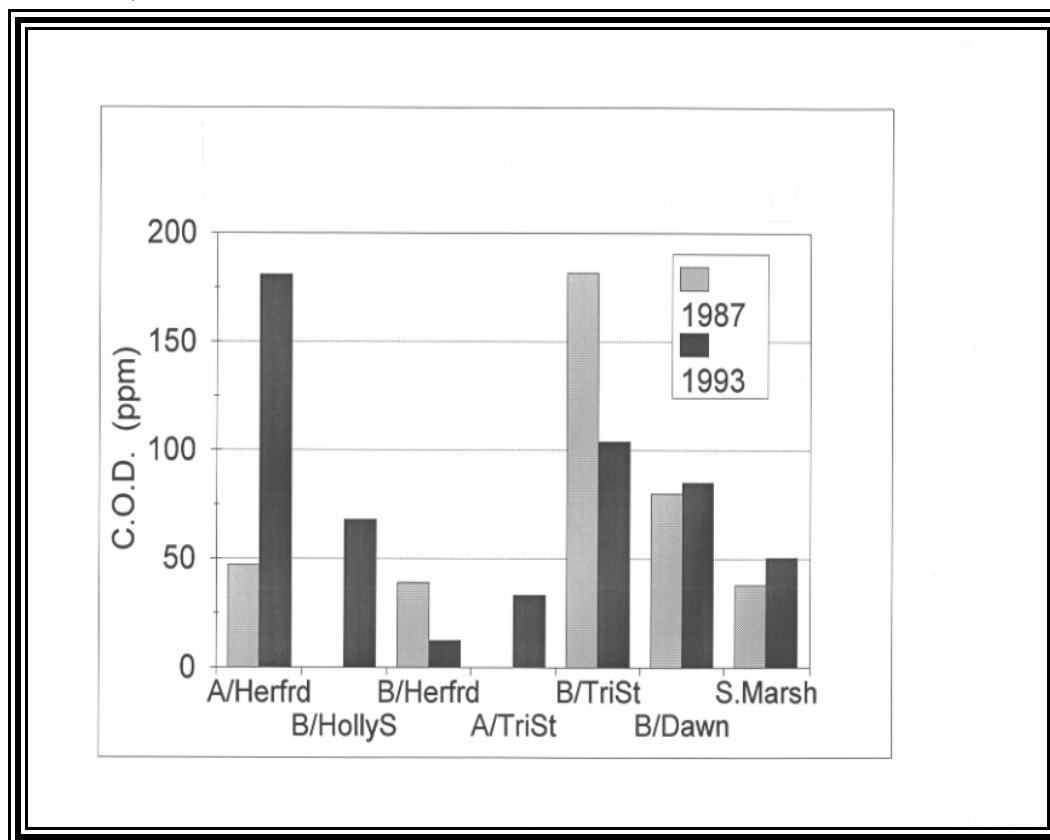
**Figure 7. Total Nitrate-Nitrogen in Tierra Blanca Creek, 1987 & 1993.** (Note: A/Herfrd is above the City of Hereford; B/HollyS is below the Holly Sugar Plant; B/Herfrd is below the City of Hereford; A/TriSt is above TriState Feedyard; B/TriSt is below TriState Feedyard; B/Dawn is below the City of Dawn; and S.Marsh is above Stewart Marsh)



**Figure 8. Ammonia-Nitrogen in Tierra Blanca Creek, 1987 & 1993.** (Note: A/Herfrd is above the City of Hereford; B/HollyS is below the Holly Sugar Plant; B/Herfrd is below the City of Hereford; A/TriSt is above TriState Feedyard; B/TriSt is below TriState Feedyard; B/Dawn is below the City of Dawn; S.Marsh is above Stewart Marsh)



**Figure 9. Chemical Oxygen Demand in Tierra Blanca Creek, 1987 & 1993.** (Note: A/Herfrd is above the City of Hereford; B/HollyS is below the Holly Sugar Plant; B/Herfrd is below the City of Hereford; A/TriSt is above TriState Feedyard; B/TriSt is below TriState Feedyard; B/Dawn is below the City of Dawn; and S.Marsh is above Stewart Marsh)



appeared to be elevated but this may be attributed to the high clay content of the sediments in the impoundments (see Table 6). Strontium and vanadium concentrations were higher in comparison to concentrations detected in water samples from Tierra Blanca Creek. TOC and COD values were below the detected concentrations in Tierra Blanca Creek. Total nitrogen levels were elevated in comparison to State screening criteria, but below concentrations detected in the creek. Organic nitrogen levels were also detected below concentrations detected in the creek. Mean ammonia-nitrogen, nitrate-nitrogen, and total phosphorus concentrations occurred below levels of concern.

The results of the nutrient and metals analyses for surface water samples collected in 1994 from the four ponds located in the Refuge are presented in Table 4. Beryllium (detection limit = 0.00004 mg/l) and selenium (detection limit = 0.002 mg/l) were below detection limits in all of the surface water samples. Aluminum concentrations were below the recommended criterion in all the ponds except Pond No. 2 (Texas Natural Resource Conservation Commission, 1996a). Boron concentrations exceeded the recommended criterion in Pond No. 1 and Pond No. 2 (U.S. Environmental Protection Agency, 1986). Iron and manganese concentrations were detected below the USEPA recommended chronic aquatic criteria in all of the ponds (U.S. Environmental Protection Agency, 1986). Detected arsenic, chromium, mercury, nickel, and zinc concentrations were below the aquatic life chronic protection criteria recommended by the State of Texas for the Prairie Dog Town Fork of the Red River (Texas Natural Resource Conservation Commission, 1996b). Copper concentrations were detected at or below the recommended aquatic life chronic protection criterion in all of the ponds (Texas Natural Resource Conservation Commission, 1996b).

**Table 4. Mean (O)\* Nutrient and Metals Concentrations in Surface Water Collected from the Four Ponds at Buffalo Lake National Wildlife Refuge, in 1994.** (Note: na is not analyzed; t is total; N/A is not applicable; and < is less than)

Analyte	Surface Water (mg/l, dissolved)				Chronic Criteria (mg/l, dissolved)
	Pond No. 1	Pond No. 2	Pond No. 3	Pond No. 4	
Al	0.03	0.22	0.02	<0.02	0.087 (a)
As	0.04	0.03	0.02	0.02	0.190 (b)
B	1.13	3.32	0.44	0.16	0.750 (c)
Ba	0.02	0.10	0.07	0.01	no criterion
Cd	0.002	0.003	0.002	0.001	$e^{[0.7852(\ln(\text{hardness}))-3.49]}$ (b)
Cr	<0.002	0.004	<0.002	0.003	0.318 (b)
Cu	0.01	0.02	0.003	0.002	0.020 (b)
Fe	0.03	0.14	0.03	0.03	1.000 (a)
Hg (t)	0.0003	0.0002	0.0002	0.0002	0.0013 t (b)
Mg	114.00	12.05	233.50	208.00	no criterion
Mn	0.01	0.01	<0.002	0.02	0.100 (c)
Mo	0.06	0.12	<0.008	<0.008	no criterion
Ni	0.002	0.007	<0.002	0.002	0.245 (b)
Pb	<0.01	0.01	0.01	0.01	$e^{[1.273(\ln(\text{hardness}))-4.705]}$ (b)
Sr	3.46	2.12	4.86	2.46	no criterion
V	0.01	0.14	0.01	0.01	no criterion
Zn	0.01	0.02	0.01	0.01	0.165 (b)
TKN	2.95	na	1.00	3.10	1.000 (d)
O-N	2.80	na	0.70	2.90	no criterion
NH <sub>3</sub> -N	0.20	na	0.28	0.22	1.000 (b)
NO <sub>3</sub> -N	0.41	na	0.30	0.33	1.000 (b)
TP	0.09	na	0.06	0.11	0.200 (b)
COD	94.80	na	78.35	90.05	no criterion
Hardness	483.00	101.00	1,130.00	951.00	N/A

\*Where concentrations were not detected above the analytical detection limit, the conservative approach of selecting the numeric value immediately below the detection limit was employed in calculating the mean.

(a) Texas Natural Resource Conservation Commission, 1996a.

(b) Texas Natural Resource Conservation Commission, 1996b.

(c) U.S. Environmental Protection Agency, 1986.

(d) U.S. Army Corps of Engineers, 1994.

Barium and magnesium concentrations were below levels of concern (Roline and Boehmke, 1981; U.S. Environmental Protection Agency, 1986). Cadmium and lead concentrations were below the State criteria in all of the ponds except Pond No. 2 (Texas Natural Resource Conservation Commission, 1996b). In addition to strontium and vanadium, criteria or screening values have also not been established for molybdenum in the State of Texas. Ammonia-nitrogen (NH<sub>3</sub>-N), nitrate-nitrogen (NO<sub>3</sub>-N), and total phosphorus (TP) concentrations were below the screening values recommended by the State of Texas in all of the ponds sampled (Texas Natural Resource Conservation Commission, 1996b). Total nitrogen (TKN) concentrations appeared to be elevated in Pond No. 1 and Pond No. 4 in comparison to screening criteria and levels detected in Tierra Blanca Creek in 1993 (U.S. Army Corps of Engineers, 1994). Organic nitrogen (O-N) levels corresponded with total nitrogen concentrations. Detected chemical oxygen demand was below the level of concern in all of the ponds sampled.

Groundwater results for samples collected in 1993 and 1994 are summarized in Table 5. Beryllium

**Table 5. Mean (O)\* Nutrient and Metals Concentrations in Groundwater Collected from Buffalo Lake National Wildlife Refuge, in 1993 and 1994.** (Note: na is not analyzed; MCL is maximum contamination level for safe drinking water; and < is less than)

Analyte	1993 (mg/l, total)	1994 (mg/l, dissolved)	Criteria (mg/l, dissolved)
Al	0.36	0.09	no criterion
As	<0.001	0.002	MCL = 0.05 (a)
B	1.89	0.70	no criterion
Ba	0.014	0.027	MCL = 2.00 (a)
Cd	<0.001	0.001	MCL = 0.005(a)
Cu	0.002	0.003	MCL = 1.00 (b)
Fe	0.74	0.12	MCL = 0.30 (b)
Mg	62.80	1.68	no criterion
Mn	0.07	0.007	MCL = 0.05 (b)
Mo	0.04	0.02	no criterion
Ni	<0.002	0.003	0.10 (c)
Sr	4.02	0.11	no criterion
Zn	0.09	0.007	MCL = 5.00 (b)
TKN	2.26	<0.20	no criterion
O-N	1.70	<0.20	no criterion
NH <sub>3</sub> -N	0.56	<0.06	1.00 (c)
NO <sub>3</sub> -N	0.36	0.45	MCL = 10.00 (a)
TOC	1.23	na	no criterion
COD	14.30	8.74	no criterion
Hardness	na	19.10	no criterion

\*Where concentrations were not detected above the analytical detection limit, the conservative approach of selecting the numeric value immediately below the detection limit was employed in calculating the mean.

(a) is primary drinking water constituent from: Texas Natural Resource Conservation Commission, 1996b.

(b) is secondary drinking water constituent from: Texas Natural Resource Conservation Commission, 1996b.

(c) recommended screening values from: Texas Natural Resource Conservation Commission, 1996b.

(detection limit = 0.0004 mg/l), chromium (detection limit = 0.002 mg/l), mercury (detection limit = 0.0002 mg/l), lead (detection limit = 0.01 mg/l), selenium (detection limit = 0.002 mg/l), and vanadium (detection limit = 0.008 mg/l) were below detection limits in all of the samples collected. Detected arsenic, barium, and cadmium concentrations were below the primary maximum contamination levels (MCLs) for drinking water established by the State of Texas for the Dockum Group Aquifer (Texas Natural Resource Conservation Commission, 1996b). Copper, iron, manganese, and zinc concentrations were detected below the secondary MCLs for drinking water (Texas Natural Resource Conservation Commission, 1996b). Nickel concentrations were below the recommended screening levels established by the State of Texas for groundwater (Texas Natural Resource Conservation Commission, 1996b). Criteria for aluminum, boron, magnesium, molybdenum, and strontium have not been developed for groundwater underlying the Refuge. Boron, molybdenum, and strontium are minor components of soil and rocks, whereas aluminum and magnesium are common components of soils and rocks that readily dissolve into solution (Texas Water Commission, 1989). Detected concentrations of these analytes may be attributed to the natural break down of the parent rock into solution within the aquifer.

Total phosphorus (TP) levels were below the detection limit of 0.02 mg/l. Nitrate-nitrogen concentrations were detected below the primary MCL while ammonia-nitrogen concentrations were detected below the recommended screening levels established by the State of Texas for groundwater (Texas Natural Resource Conservation Commission, 1996b). Criteria for total nitrogen (TKN), organic nitrogen (O-N), total organic carbon (TOC), and chemical oxygen demand (COD) have not been established for groundwater; however, detected concentrations of these constituents in groundwater do not appear to warrant concern. Based on

the results of the analyses, infiltration of contaminants into the groundwater does not appear to be a cause for significant concern at the Refuge.

The analytical results in mg/kg dry weight for sediments collected from the four ponds at the Refuge in 1994 are summarized in Table 6. The sediments in Pond No. 1 and Pond No. 2 were dominated by clays,

<b>Table 6. Mean (O)* Nutrient and Metals Concentrations in Sediments Collected from the Four Ponds at Buffalo Lake National Wildlife Refuge, in 1994.</b> (Note: N/A is not applicable; < is less than)					
Analyte	Sediment (mg/kg dry weight)				Criteria (mg/kg dry weight)
	Pond No. 1	Pond No. 2	Pond No. 3	Pond No. 4	Reservoirs
Al	21,155.10	38,574.40	18,623.80	17,939.34	no criterion
As	5.42	8.51	4.10	4.75	17.6 (a)
B	20.93	54.30	13.90	13.22	no criterion
Ba	179.29	245.71	217.22	181.86	287.0 (a)
Be	0.62	1.25	0.69	0.66	no criterion
Cd	0.43	0.58	0.43	0.47	2.0 (a)
Cr	14.64	26.39	13.98	13.72	34.0 (a)
Cu	10.80	17.20	10.39	9.95	33.0 (a)
Fe	12,602.93	20,572.48	11,875.49	11,530.35	20,000 - 40,000 (b)
Hg	0.07	<0.04	<0.04	<0.04	0.16 (a)
Mg	10,397.29	16,267.83	10,365.54	7,984.15	no criterion
Mn	253.56	411.49	266.29	195.65	1,210.0 (a)
Ni	10.54	21.66	11.36	10.62	25.0 (a)
Pb	7.91	14.57	8.69	9.19	61.5 (a)
Se	<0.19	<0.19	0.41	0.38	1.73 (a)
Sr	423.81	698.18	338.96	227.44	no criterion
V	35.41	65.43	35.63	44.32	no criterion
Zn	35.48	57.72	32.46	31.64	120.0 (a)
TKN	2,670.00	4,420.00	1,114.50	2,515.00	550.0 - 4,800.0 (b)
O-N	2,465.00	3,980.00	1,030.00	2,435.00	3,896.0 (c)
NH <sub>3</sub> -N	205.00	440.00	82.50	79.50	no criterion
NO <sub>3</sub> -N	1.90	4.42	<1.45	<1.50	no criterion
TP	4.15	<1.00	3.70	3.24	600.0 - 2,000.0 (b)
% TOC	0.57	0.43	0.33	0.88	1.00 - 10.00 (b)
% TVS	4.28	5.42	3.56	3.73	no criterion
% Sand	38.0	16.0	34.0	38.0	N/A
% Silt	15.0	17.0	27.0	25.0	N/A
% Clay	47.0	67.0	39.0	37.0	N/A

\*Where concentrations were not detected above the analytical detection limit, the conservative approach of selecting the numeric value immediately below the detection limit was employed in calculating the mean.

(a) Texas Natural Resource Conservation Commission. 1996.

(b) Persaud *et al.*, 1993.

(c) Irwin *et al.*, 1996.

whereas the sediments in Pond No. 3 and Pond No. 4 were predominately composed of sand and clay. Molybdenum concentrations were below the detection limits in all of the samples collected (detection limits ranged from 1.32 - 1.89 mg/kg dry weight). Arsenic, barium, cadmium, chromium, copper, manganese, mercury, nickel, selenium, and zinc concentrations were all below the recommended aquatic life chronic

criteria developed for sediments in reservoirs by the State of Texas (Texas Natural Resource Conservation Commission, 1996b). Iron concentrations were below the Ontario lowest effects level (LEL) of 20,000.0 mg/kg dry weight in sediments collected from all of the ponds except Pond No. 2; however the detected concentration in Pond No. 2 was well below the Ontario severe effects level (SEL) of 40,000.0 mg/kg dry weight (Persaud *et al.*, 1993). The LEL indicates a level of sediment contamination which can be tolerated by a majority of benthic organisms whereas the SEL is indicative of contaminated sediments that would be detrimental to a majority of benthic organisms (Persaud *et al.*, 1993). Aluminum, beryllium, boron, and vanadium concentrations were comparable with sediments collected from an undisturbed playa ( $\bar{O}$  = 29,650.0 mg/kg dry weight;  $\bar{O}$  = 1.36 mg/kg dry weight;  $\bar{O}$  = 28.0 mg/kg dry weight; and  $\bar{O}$  = 43.78 mg/kg dry weight, respectively) in the Texas Panhandle by Irwin and others (1996). Magnesium concentrations were comparable to concentrations in sediment samples collected from a naturally saline playa ( $\bar{O}$  = 22,682.50 mg/kg dry weight) in the same area (Irwin *et al.*, 1996). Strontium concentrations in samples collected from all four ponds were comparable to levels detected by Irwin and others (1996) in sediments collected from CAFO waste lagoons ( $\bar{O}$  = 168.0 mg/kg dry weight).

Total phosphorus (TP) and total organic carbon (%TOC) concentrations were below the Ontario LEL values (Persaud *et al.*, 1993). Organic nitrogen levels were below the recommended benthic fauna protection criterion (Irwin *et al.*, 1996) in sediments collected from all of the ponds except Pond No. 2. Total nitrogen (TKN) concentrations were above the Ontario LEL but below the SEL values in all four ponds (Persaud *et al.*, 1993). Levels of organic matter (%TVS) were comparable to sediments collected from an undisturbed playa ( $\bar{O}$  = 5.91) in the Texas Panhandle by Irwin and others (1996). Ammonia-nitrogen ( $\text{NH}_3\text{-N}$ ) levels in sediments collected from Pond No. 1 and Pond No. 2 were comparable to levels detected by Irwin and others (1996) in sediments collected from CAFO waste lagoons ( $\bar{O}$  = 614.25 mg/kg dry weight), whereas ammonia-nitrogen concentrations detected in sediments from Pond No. 3 and Pond No. 4 were comparable to sediments collected from an undisturbed playa ( $\bar{O}$  = 83.93 mg/kg dry weight) (Irwin, *et al.*, 1996). Nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) concentrations detected in sediments from Pond No. 3 and Pond No. 4 were also comparable to sediments collected by Irwin and others (1996) from an undisturbed playa ( $\bar{O}$  = 2.28 mg/kg dry weight).

Sediment samples collected from Pond No. 1 and Pond No. 2 were also analyzed in mg/kg dry weight for total-PCB content and organochlorine pesticide residues. In sediment collected from Pond No. 1, the analytical detection limit for total-PCBs and the organochlorine compound, toxaphene was 0.072 mg/kg dry weight, while the analytical detection limit for the remaining 18 organochlorine compounds was 0.014 mg/kg dry weight. In Pond No. 2, the analytical detection limit for total-PCBs and toxaphene was 0.088 mg/kg dry weight, while the analytical detection limit for the remaining 18 organochlorine compounds was 0.018 mg/kg dry weight. None of the organochlorine compounds analyzed, including total-PCBs, were detected in concentrations above the respective analytical detection limits in any of the sediment samples collected.

Analytical results in mg/kg dry weight for soil samples collected at the Refuge in 1993 are summarized in Table 7. Molybdenum (detection limits ranged from 1.06 - 5.96 mg/kg dry weight) and selenium (detection limits ranged from 0.22 - 1.13 mg/kg dry weight) were below the analytical detection limits in all of the samples. Aluminum, arsenic, barium, chromium, lead, mercury, and vanadium concentrations were all detected below the median concentrations in U.S. soils. Beryllium, boron, copper, iron, magnesium, manganese, nickel, strontium, and zinc concentrations were detected in excess of the U.S. soil median values, but well within the background range values. Detected cadmium concentrations exceeded the United States median concentration of 0.05 mg/kg dry weight (U.S. Environmental Protection Agency, 1980). However, the detected concentration was less than the recommended screening benchmark value of 20.0 mg/kg dry weight (Efroymson *et al.*, 1997).

**Table 7. Comparison of Metals Concentrations of Soils Collected in Buffalo Lake National Wildlife Refuge in 1993 with Background Concentrations in Soils of the United States.** (Note: DR is detection ratio to number of samples; Min is minimum detected concentration; GMEAN is geometric mean; O is mean detected concentration; Max is maximum detected concentration; < is less than; and ---- is data unavailable)

ANALYTE	Buffalo Lake NWR Soils (mg/kg dry weight)					U.S. Background Soils* (mg/kg dry weight)	
	DR	Min	GMEAN	O	Max	GMEAN	Background
Al	24/24	19,672	38,724	39,879	54,989	47,000	5,000 - 100,000
As	18/24	0.1	0.6	0.8	1.7	5.5	1.2 - 22
B	24/24	16	28.1	29.3	44.5	23	5.8 - 91
Ba	24/24	138	251	256	342	580	200 - 1,700
Be	24/24	0.6	1.2	1.3	1.6	0.7	0.13 - 3.6
Cd	5/24	< 0.5	0.4	---	0.8	----	----
Cr	24/24	14.2	28.3	29.3	41.3	41	8.5 - 200
Cu	24/24	13.4	23.9	24.2	31.3	21	4.9 - 90
Fe	24/24	10,634	23,074	23,876	30,958	18,000	100 - 100,000
Pb	24/24	6.1	15.5	16.4	24.2	17	5.2 - 55
Mg	24/24	7,672	14,848	15,089	20,320	4,400	500 - 100,000
Mn	24/24	213	431	442	584	380	97 - 1,500
Hg	20/24	<0.001	0.02	0.02	0.06	0.05	0.01 - 0.25
Ni	24/24	9.2	19.1	20.3	54.0	15	3.4 - 66
Sr	24/24	232.8	330.1	334.5	430.5	200	43 - 930
V	24/24	31.3	60.4	62.4	61.3	70	18 - 270
Zn	24/24	43.3	86.1	92.8	319.0	55	17 - 180

\* Shacklette and Boerngen, 1984.

Contaminant concentrations detected in soils collected from the three cropping treatments were statistically compared to the soil samples collected in the 1987 Phase I study using the nonparametric Kruskal-Wallis Test. A one-way analysis of variance (ANOVA) was used to determine if soil contaminant concentrations from different treatments were significantly different at an error level of 5.0%. If the population variances were significantly different, then a Tukey's Honestly Significant Difference (HSD) Test was employed to determine if the mean (O) of the treatments were different. The results of this analysis are summarized in Table 8.

Among the three cropping treatments, there were no statistically significant differences in aluminum, arsenic, boron, barium, copper, iron, lead, nickel, strontium, vanadium, zinc, total nitrogen (TKN), organic nitrogen (O-N), ammonia nitrogen (NH<sub>3</sub>-N) and total phosphorus (TP) concentrations. Beryllium, chromium, magnesium, and manganese concentrations detected in the sudan fields were not statistically

**Table 8. Results of ANOVA and Tukey's HSD Test of Means (O) from the Comparison Between the Three 1993 Soil Cropping Treatments and the 1987 Soils Data, Buffalo Lake National Wildlife Refuge.** (Note: row means (O) that share the same capital letter are not significantly different; ---- is data unavailable; and < is less than)

Analyte	Soil Treatment O (mg/kg dry weight)				ANOVA Results
	1987	Fallow	Wheat	Sudan	[F(degrees freedom), P]
Al	11562 A	34247 B	40600 B	44788 B	F(3,24)=12.9, P= <0.001
As	----	0.57 B	0.76 B	0.99 B	F(2,21)=1.6, P=0.23
B	----	25.9 A	27.7 A	34.2 A	F(2,21)=2.6, P=0.10
Ba	207.3 A	226.7 AB	256.1 AB	281.6 B	F(3,24)=3.5, P=0.03
Be	0.84 A	1.07 AB	1.31 BC	1.38 C	F(3,24)=7.0, P=(0.015)
Cr	10.1 A	24.8 B	29.7 BC	33.5 C	F(3,24)=14.8, P= <0.001
Cu	12.0 A	24.7 B	23.6 B	24.3 B	F(3,24)=11.3, P= <0.001
Fe	10520 A	20121 B	25088 B	26419 B	F(3,24)=11.8, P= <0.001
Pb	14.3 A	13.5 A	17.5 A	18.1 A	F(3,24)=2.1, P=0.13
Mg	12738 A	12860 A	15112 AB	17296 B	F(3,24)=5.6, P=0.005
Mn	382.8 AB	375.7 A	456.6 AB	494.2 B	F(3,24)=4.1, P=0.02
Ni	11.8 A	16.5 A	23.9 A	20.5 A	F(3,24)=2.9, P=0.06
Sr	429.5 A	343.9 A	309.0 A	350.5 A	F(3,24)=1.5, P=0.23
V	13.9 A	53.7 B	61.8 B	71.6 B	F(3,24)=18.4, P= <0.001
Zn	37.0 A	74.5 AB	89.9 AB	114.0 B	F(3,24)=2.8, P=0.06
TKN	1405 A	2200 A	2287 A	2262 A	F(3,24)=2.5, P=0.08
O-N	1400 A	2185 A	2273 A	2251 A	F(3,24)=2.4, P=0.08
NH <sub>3</sub> -N	2.7 A	24.0 B	24.6 B	20.6 AB	F(3,24)=3.5, P=0.03
NO <sub>3</sub> -N	7.0 A	1 BC	155.3 C	82.0 AB	F(3,24)=9.2, P= <0.001
TP	744 A	1.6 B	3.1 B	1.7 B	F(3,24)=498, P= <0.001
%TOC	----	2.1 A	1.7 AB	1.6 B	F(2,21)=4.0, P=0.03
%TVS	5.1 A	7.3 A	7.9 AB	7.3 B	F(3,24)=6.1, P=0.03

higher than the concentrations detected in the wheat fields, but were higher than concentrations detected in the fallow fields. Aluminum, chromium, copper, iron, and vanadium concentrations were statistically higher in soils collected in 1993 than in soils collected in 1987. There were no significant differences between barium, magnesium, manganese, and zinc concentrations detected in soils collected in 1987 and soils collected from the fallow and wheat fields in 1993. There were also no differences between beryllium concentrations detected in soils collected in 1987 and soils collected from the fallow fields in 1993. Detected ammonia-nitrogen concentrations in soils collected in 1987 were not statistically significantly different than soils collected in the sudan fields, but were statistically lower than detected concentrations in soils collected from the fallow and wheat fields. Total phosphorus concentrations were statistically higher in soils collected in 1987 than in soils collected from the three cropping treatments in 1993. There were no statistically significant differences in lead, nickel, strontium, total nitrogen, and organic nitrogen concentrations between the soils collected in 1987 and the soils collected in 1993. In nitrate-nitrogen (NO<sub>3</sub>-N) levels, there were no statistically significant differences between the soils collected in 1987 and the soils collected in the sudan fields in 1993; no significant difference between the soils collected in the fallow and sudan fields; and no differences between soils collected in the fallow and wheat fields. However, quantitatively, the detected nitrate concentrations in the wheat fields were 20 times higher than concentrations detected in the 1987 soils; 150 times higher than detected concentrations in the fallow fields; and almost two times greater than the detected concentration in sudan fields.

Results in mg/kg dry weight of soils data collected at the moist soil management units in Stewart Marsh in 1994 are presented in Table 9. The soil in these moist soil management units appeared to be dominated

<b>Table 9. Mean (O)* Nutrient and Metals Concentrations (in mg/kg dry weight) in Soils Collected from the Five Moist Soil Management Units, Buffalo Lake National Wildlife Refuge, in 1994.</b> (Note: < is less than)					
Analyte	MSMU No. 1	MSMU No. 2	MSMU No. 3	MSMU No. 4	MSMU No. 5
Al	29,817.10	27,856.59	23,982.78	32,701.40	25,864.07
As	5.53	5.48	4.65	5.47	4.73
B	17.60	15.54	14.35	17.75	17.14
Ba	192.35	155.79	162.02	208.47	144.09
Be	1.036	1.01	0.91	1.18	0.88
Cd	0.482	0.55	0.47	0.61	0.435
Cr	20.37	19.56	16.75	21.58	17.85
Cu	14.61	14.13	12.86	16.72	12.52
Fe	16,975.14	16,682.43	14,988.34	19,136.08	14,574.69
Hg	<0.04	<0.04	<0.04	0.054	<0.04
Mg	9,006.71	7,705.96	7,074.46	9,497.65	7,019.45
Mn	340.49	280.60	282.99	373.37	268.51
Ni	14.88	14.53	13.23	16.99	12.83
Pb	12.68	14.24	10.82	16.09	11.31
Se	0.21	<0.19	<0.19	<0.19	<0.19
Sr	139.51	110.35	110.85	149.84	121.80
V	43.51	39.59	33.95	41.98	37.77
Zn	51.17	54.13	45.02	61.75	45.85
TKN	12,154.0	8,200.0	20,550.0	34,000.0	9,530.0 (a)
O-N	11,816.0	7,910.0	19,850.0	33,000.0	25,100.0 (a)
NH <sub>3</sub> -N	327.0	290.0	670.0	995.0	610.0
NO <sub>3</sub> -N	2.23	16.20	11.72	32.75	16.0
TP	1.95	0.99	<1.00	2.17	0.97
% TOC	1.12	1.46	1.14	1.78	1.09
% TVS	5.94	5.69	5.42	7.88	5.57
% Sand	28.4	32.0	34.0	22.0	38.0
% Silt	20.6	25.0	25.0	25.0	23.0
% Clay	51.0	43.0	41.0	53.0	39.0

\*Where concentrations were not detected above the analytical detection limit, the conservative approach of selecting the numeric value immediately below the detection limit was employed in calculating the mean.

(a) Data excluded from interpretation because results are suspect. Organic nitrogen is a component of total nitrogen therefore the detected concentration should be less than the detected total nitrogen concentration.

by clays. Molybdenum was not found above the detection limit in any of the soil samples collected from the moist soil management units (detection limits ranged from 1.05 - 1.42 mg/kg dry weight). Aluminum, arsenic, boron, barium, chromium, copper, iron, mercury, nickel, lead, selenium, and vanadium concentrations were all detected below the respective median concentrations for soils in the United States

(Shacklette and Boerngen, 1984). Beryllium concentrations exceeded the United States soil median value of 0.63 mg/kg dry weight but fell within the background range of <1.0 - 15.0 mg/kg dry weight (Shacklette and Boerngen, 1984). Cadmium concentrations exceeded the United States median concentration of 0.05 mg/kg dry weight (U.S. Environmental Protection Agency, 1980). However, as with the soils from the cropping treatments, detected cadmium concentrations were less than the recommended screening benchmark value of 20.0 mg/kg dry weight (Efroymson *et al.*, 1997).

Detected total nitrogen (TKN), organic nitrogen (O-N), and ammonia-nitrogen (NH<sub>3</sub>-N) concentrations were higher in the moist soil management units than in soils collected from the cropping treatments in the dry reservoir bed. Total phosphorus (TP), total organic carbon (%TOC), and organic matter (%TVS) levels were comparable with levels detected in soils from the cropping treatments. Nitrate-nitrogen (NO<sub>3</sub>-N) concentrations were lower in the moist soil management units than concentrations detected in the dry reservoir bed.

A composite soil sample from MSMU No. 2 was also analyzed in mg/kg dry weight for total-PCB content and organochlorine pesticide residues. The analytical detection limit for total-PCBs and the organochlorine compound, toxaphene was 0.062 mg/kg dry weight, while the analytical detection limit for the remaining 18 organochlorine compounds was 0.012 mg/kg dry weight. None of the organochlorine compounds analyzed, including total-PCBs, were detected in concentrations above the respective analytical detection limits in any of the sediment samples collected.

The results of the metals analyses in mg/kg dry weight for plant tissues collected from the cropping treatments in the dry reservoir bed of the Refuge are summarized in Table 10. Beryllium (detection limits ranged from 0.05 - 0.22 mg/kg dry weight), lead (detection limits ranged from 1.22 - 5.41 mg/kg dry weight), and mercury (detection limits ranged from 0.025 - 0.108 mg/kg dry weight) were below the detection limits. Mean aluminum, arsenic, boron, barium, chromium, copper, iron, magnesium, manganese, molybdenum, nickel, strontium, and vanadium concentrations were all detected below the recommended dietary concentrations protective of wildlife (National Research Council, 1980). Mean cadmium concentrations were detected below the predator protection limit; however, the maximum detected cadmium concentration was detected at the predator protection limit (Eisler, 1985). Mean selenium and zinc concentrations were also detected below dietary concentrations protective of wildlife (Lemly, 1993; Eisler, 1993).

Metal contaminants detected in *Kochia* and sudan grass collected from the three cropping treatments were statistically analyzed using the nonparametric Kruskal-Wallis Test. A one-way analysis of variance (ANOVA) was used to determine if plant contaminant concentrations from different treatments were significantly different at an error level of 5.0%. If the population variances were significantly different, then a Tukey's Honestly Significant Difference (HSD) Test was employed to determine if the mean (O) of the treatments was also different. The results of this statistical analysis are summarized in Table 11.

There were no statistically significant differences in cadmium, chromium, copper, nickel, selenium, and zinc concentrations detected in the two plant species collected from the three cropping treatments. Detected aluminum, iron, manganese, and vanadium concentrations were statistically higher in *Kochia* collected from the wheat fields than in *Kochia* collected from the fallow fields and sudan grass collected from the sudan fields. Boron, barium, magnesium, and strontium concentrations were statistically higher in the *Kochia* collected from the fallow and the wheat fields than in the sudan grass collected from the sudan fields. Detected molybdenum concentrations were statistically higher in sudan grass collected from the sudan fields than *Kochia* collected from the other two treatments. Arsenic concentrations were statistically higher in *Kochia* collected from the fallow fields and sudan grass collected from the sudan fields than in *Kochia* collected from the wheat fields.

**Table 10. Comparison of Metals Concentrations (mg/kg, dry weight) in Plant Tissues Collected from Buffalo Lake National Wildlife Refuge in 1993 with Diagnostic Concentrations Considered Protective of Wildlife.** (Note: DR is detection ratio; Min is minimum detected concentration; O is mean detected concentration; STD is standard deviation; Max is maximum detected concentration; and < is less than)

Analyte	Buffalo Lake NWR Plant Tissue O				Diagnostic Criteria	
	DR	Min	O $\pm$ STD	Max	Conc*	Reference
Al	23/23	9.6	240.7 $\pm$ 389.0	1,358.4	926.0	(a)
As	20/23	0.03	2.5 $\pm$ 2.2	9.0	140.0	(b)
B	23/23	8.4	31.2 $\pm$ 15.7	57.1	140.0	(a)
Ba	23/23	9.7	37.2 $\pm$ 21.7	70.8	93.0	(a)
Cd	12/23	0.1	0.3 $\pm$ 0.1	0.5	0.5	(c)
Cr	19/23	0.3	0.8 $\pm$ 0.5	2.3	24.0	(a)
Cu	23/23	4.3	6.5 $\pm$ 1.4	9.0	116.0	(a)
Fe	23/23	43.8	181.4 $\pm$ 191.7	876.1	2,300.0	(a)
Mg	23/23	2,216.0	5,617.0 $\pm$ 2,589.0	10,000.0	14,000.0	(a)
Mn	23/23	17.7	4.0 $\pm$ 21.3	10.5	1,850.0	(a)
Mo	15/23	0.7	2.1 $\pm$ 1.2	4.8	46.0	(a)
Ni	18/23	0.4	0.9 $\pm$ 0.1	1.6	230.0	(a)
Se	11/23	0.3	1.0 $\pm$ 0.6	2.8	3.0	(d)
Sr	23/23	33.0	155.2 $\pm$ 90.8	298.3	9,300.0	(a)
V	9/23	<0.3	0.4 $\pm$ 0.6	2.6	46.0	(a)
Zn	23/23	16.4	24.4 $\pm$ 4.4	34.7	178.0	(e)

\*The protective dietary concentration reported for the most sensitive species (in wet weight) was converted to a dry-weight concentration using the average grasshopper moisture content (78.41%). For example, a protective dietary concentration of 200 mg/kg for poultry was reported by the National Research Council;  $200 \div [1 - (78.41 \div 100)] = 926$  mg/kg dry weight.

(a) National Research Council, 1980.

(b) Eisler, 1994.

(c) Eisler, 1985.

(d) Lemly, 1993.

(e) Eisler, 1993.

Analytical results in mg/kg wet weight for the metals and organochlorine analyses for fish collected from Stewart Marsh are summarized in Table 12. Analytical results in mg/kg wet weight are also summarized in Table 12 for metals detected in vegetation collected from the five moist soil management units.

**Table 11. Results of ANOVA and Tukey's HSD Test of Means (O) of Plants Collected from Three Cropping Treatments at Buffalo Lake National Wildlife Refuge, in 1993.** (Note: row mean (O) that share the same capital letter are not significantly different; and < is less than)

Analyte	Buffalo Lake Plant Tissue O (mg/kg dry weight)			ANOVA Results
	Fallow	Wheat	Sudan	[F(degrees freedom), P]
Al	69.8 A	628.9 B	71.9 A	F(2,20)=8.4, P=0.002
As	4.5 A	1.2 B	1.7 A	F(2,20)=8.4, P=0.002
B	39.2 A	42.6 A	13.1 B	F(2,20)=29.6, P= <0.001
Ba	47.0 A	51.8 A	14.7 B	F(2,20)=15.4, P=0.0001
Cd	0.2 A	0.3 A	0.3 A	F(2,20)=1.0, P=0.39
Cr	0.5 A	1.0 A	0.9 A	F(2,20)=1.9, P=0.17
Cu	5.6 A	7.2 A	6.7 A	F(2,20)=3.4, P=0.05
Fe	79.7 A	362.9 B	124.3 A	F(2,20)=7.2, P=0.004
Mg	6,771.6 A	7,460.1 A	2,848.9 B	F(2,20)=18.5, P= <0.001
Mn	38.0 A	63.9 B	29.8 A	F(2,20)=8.8, P=0.00018
Mo	1.5 A	1.8 A	3.1 B	F(2,20)=6.1, P= <0.01
Ni	0.8 A	0.9 A	0.8 A	F(2,20)=0.2, P=0.83
Se	1.1 A	0.7 A	1.0 A	F(2,20)=1.5, P=0.26
Sr	211.2 A	199.8 A	60.1 B	F(2,20)=15.9, P= <0.001
V	0.1 A	1.0 B	0.2 A	F(2,20)=8.4, P=0.002
Zn	21.6 A	24.9 A	26.6 A	F(2,20)=3.2, P=0.06

Beryllium (detection limit = 0.02 mg/kg wet weight), cadmium (detection limit = 0.06 mg/kg wet weight), lead (detection limit = 0.50 mg/kg wet weight), and molybdenum (detection limit = 0.40 mg/kg wet weight) were below the detection limits in all the catfish samples analyzed. Arsenic concentrations were detected below the recommended predator protection limit (Eisler, 1994). Detected aluminum, barium, copper, iron, magnesium, manganese, nickel, strontium, and vanadium concentrations were below the predator protection limits for avian species developed from dietary levels recommended by the National Research Council (1980). Boron concentrations were below the predator protection limit recommended by Eisler (1990). Chromium levels detected were also below the predator protection limit for avian species recommended by Eisler (1986). Detected mercury concentrations were below the mammalian and avian predator protection limits (Eisler, 1987). Selenium concentrations were detected below the predator protection limit recommended by Lemly (1986), while detected zinc concentrations were below the level harmful to avian predators recommended by Eisler (1993).

**Table 12. Mean (O)\* Concentrations of Metals and Organochlorines in Biological Samples Collected from Stewart Marsh and the Five Moist Soil Management Units at Buffalo Lake National Wildlife Refuge, in 1994** (Note: bdl is below detection limit; na is not analyzed)

Analyte	Black Bullheads (mg/kg wet weight)	Vegetation (mg/kg wet weight)
	Stewart Marsh	Moist Soil Management Units
Al	44.73	29.62
As	0.073	0.13
B	0.47	7.93
Ba	4.22	37.32
Cr	0.33	bdl
Cu	0.56	1.02
Fe	47.48	25.52
Hg	0.028	0.01
Mg	337.25	1,430.00
Mn	5.25	10.59
Mo	bdl	0.72
Ni	0.14	0.38
Se	0.21	0.29
Sr	40.65	37.92
V	0.26	0.04
Zn	17.18	4.36
<i>p,p'</i> -DDE	0.0275	na

\*Where concentrations were not detected above the analytical detection limit, the conservative approach of selecting the numeric value immediately below the detection limit was employed in calculating the mean.

Of the 20 organochlorine compounds analyzed, only one, *p,p'*-DDE, was detected above the analytical detection limit. DDE is a residual metabolite of the pesticide DDT which was banned in the United States in 1972. Detection of DDT metabolites with a corresponding lack of DDT detections is indicative of a low rate of influx and demonstrates a continued weathering of residual DDT (Moring, 1997). DDE has a biological half life of eight years and is listed by the USEPA as a possible carcinogen (U.S. Environmental Protection Agency, 1994). Detected levels of *p,p'*-DDE were below the National Academy of Sciences/National Academy of Engineering recommended fish-eating wildlife protection criteria of 1.0 mg/kg wet weight (Nowell and Resek, 1994).

In plants collected from the moist soil management units, beryllium (detection limit = 0.02 mg/kg wet weight), cadmium (detection limit = 0.06 mg/kg wet weight), chromium (detection limit = 0.10 mg/kg wet weight), and lead (detection limit = 0.50 mg/kg wet weight) were below the analytical detection limits in all of the samples collected. Only one composite sample, which was collected from MSMU No. 3, contained detectable mercury levels, and the concentration detected was at the analytical detection limit of 0.01 mg/kg wet weight. Aluminum, arsenic, boron, chromium, copper, iron, magnesium, manganese, nickel, strontium, vanadium, and zinc concentrations were detected below levels of concern. Barium levels appeared to be elevated but not to a point of concern.

Detected metal concentrations in mg/kg wet weight, from biological samples collected in 1994 from Pond No. 1, Pond No. 3, and Pond No. 4 are summarized in Table 13. Molybdenum concentrations were below

**Table 13. Mean (O)\* Metals Concentrations in Composite Biological Samples Collected from the Four Ponds at Buffalo Lake National Wildlife Refuge, in 1994.** (Note: < is less than)

Analyte	Damselfly Larvae (mg/kg wet weight)			Tadpole (mg/kg wet wt.)	Aquatic Vegetation (mg/kg wet weight)		
	Pond 1	Pond 3	Pond 4	Pond 3	Pond 1	Pond 3	Pond 4
Al	23.10	26.70	5.81	1,500.00	94.47	160.70	20.40
As	0.31	0.42	0.30	0.89	1.50	5.26	1.33
B	1.89	1.63	0.77	3.89	11.46	41.86	34.10
Ba	2.02	0.50	2.00	20.40	18.17	4.36	3.98
Be	<0.02	<0.02	<0.02	0.05	<0.02	<0.02	<0.02
Cd	0.07	<0.06	<0.06	<0.06	0.053	<0.06	<0.06
Cr	<0.10	<0.10	<0.10	1.22	0.15	0.14	<0.1.0
Cu	1.07	1.61	1.15	0.93	1.02	1.26	1.85
Fe	21.03	23.95	8.72	974.00	60.70	97.00	21.70
Hg	0.07	0.04	0.05	<0.01	0.01	<0.01	<0.01
Mg	220.33	365.00	244.67	1,680.00	1,212.70	6,539.33	2,367.33
Mn	1.79	1.47	1.26	29.5	44.83	12.67	61.67
Ni	0.16	0.20	0.13	0.90	0.38	0.46	0.82
Pb	<0.50	<0.50	<0.50	0.74	<0.50	<0.50	<0.50
Se	0.41	0.54	<0.10	0.59	<0.20	0.21	0.21
Sr	12.55	5.57	6.18	45.9	362.23	33.73	27.8
V	0.07	0.11	<0.05	2.86	0.18	2.75	0.22
Zn	8.32	8.98	7.10	5.41	3.67	3.43	4.36

\*Where concentrations were not detected above the analytical detection limit, the conservative approach of selecting the numeric value immediately below the detection limit was employed in calculating the mean.

the analytical detection limits in all of the biological samples collected (detection limits ranged from 0.39 - 0.45 mg/kg wet weight). In the composite damselfly larvae samples, beryllium, chromium, and lead concentrations were not detected above the analytical detection limits. Detected aluminum, arsenic, boron, barium, cadmium, copper, iron, mercury, magnesium, manganese, nickel, selenium, strontium, vanadium, and zinc concentrations were below levels of concern for predatory wildlife species. In the composite tadpole samples collected from Pond No. 3, cadmium and mercury concentrations were below the analytical detection limit. Arsenic, beryllium, boron, chromium, copper, iron, magnesium, manganese, nickel, lead, selenium, strontium, vanadium, and zinc were detected below levels of concern for predatory species. Detected aluminum and barium concentrations were elevated within the tadpole samples. In the aquatic vegetation collected from Pond No. 1, Pond No. 3, and Pond No. 4, beryllium and lead concentrations

were below the analytical detection limits. Detected aluminum, arsenic, barium, chromium, copper, iron, mercury, manganese, nickel, selenium, strontium, vanadium, and zinc were below levels of concern. Elevated levels of boron and magnesium were detected in the aquatic vegetation samples collected from Pond No. 3 and Pond No. 4. Elevated levels of cadmium were detected in the vegetation sampled from Pond No. 1.

Results of the metals analyses in mg/kg dry weight for terrestrial invertebrates (grasshoppers) collected from the Refuge in 1993 are summarized in Table 14. Beryllium (detection limit = 0.07 mg/kg dry weight),

<b>Table 14. Comparison of Metals Concentrations (mg/kg, dry weight) in Grasshoppers Collected from Buffalo Lake National Wildlife Refuge in 1993 with Diagnostic Concentrations Considered Protective of Wildlife.</b> (Note: DR is detection ratio; Min is minimum detected concentration; O is mean detected concentration; STD is standard deviation; Max is maximum detected concentration; ---- is data unavailable; and < is less than)						
Analyte	Buffalo Lake NWR Grasshoppers				Diagnostic Criteria	
	DR	Min	O ± STD	Max	Conc*	Reference
Al	6/6	24.3	73.2 ± 60.8	167.9	715.0	(a)
As	6/6	0.6	1.4 ± 0.8	2.6	100.0	(b)
B	6/6	19.3	23.9 ± 4.8	32.7	100.0	(a)
Ba	6/6	3.4	17.6 ± 9.5	27.7	70.0	(a)
Cd	3/6	<0.2	0.2 ± 0.1	0.4	0.4	(c)
Cr	3/6	0.5	0.6 ± 0.1	0.7	24.0	(a)
Cu	6/6	42.6	64.3 ± 12.2	74.9	90.0	(a)
Fe	6/6	87.0	117.4 ± 40.7	188.3	1,800.0	(a)
Mg	6/6	964.5	1,316.0 ± 315.5	1,709.6	10,800.0	(a)
Mn	6/6	7.7	12.0 ± 3.2	15.8	1,400.0	(a)
Mo	3/6	<0.8	2.0 ± 1.4	3.7	36.0	(a)
Ni	6/6	0.6	0.8 ± 0.2	1.0	180.0	(a)
Se	6/6	1.0	2.1 ± 0.6	2.7	3.0	(d)
Sr	6/6	23.6	56.1 ± 27.7	101.1	7,200.0	(a)
V	6/6	0.2	0.4 ± 0.2	0.7	36.0	(a)
Zn	6/6	123.4	131.0 ± 8.6	146.8	178.0	(e)

\*The protective dietary concentration reported for the most sensitive species (in wet weight) was converted to a dry-weight concentration using the average grasshopper moisture content (72.03%). For example, a protective dietary concentration of 200 mg/kg for poultry was reported by the National Research Council;  $200 \div [1 - (74.02 \div 100)] = 715 \text{ mg/kg dry weight}$ .

(a) National Research Council, 1980.

(b) Eisler, 1994.

(c) Eisler, 1985.

(d) Lemly, 1993.

(e) Eisler, 1993.

lead (detection limits ranged from 1.70 - 1.87 mg/kg dry weight), and mercury (detection limits ranged from 0.034 - 0.038 mg/kg dry weight) concentrations were below the analytical detection limits in all of the composite grasshopper samples collected. The remaining metals were detected below levels of concern for predatory avian species.

Metal contaminants detected in grasshoppers collected from the fallow field and sorghum field cropping treatments were statistically analyzed using the nonparametric Kruskal-Wallis Test. A one-way ANOVA was used to determine if grasshopper contaminant concentrations from different treatments were significantly different at an error level of 5.0%. If the population variances were significantly different, then a Tukey's HSD Test was employed to determine if the mean (O) of the treatments were different. The results of this statistical analysis are summarized in Table 15.

<b>Table 15. Results of ANOVA and Tukey's HSD Test of Means of Grasshoppers Collected from Two Cropping Treatments at Buffalo Lake National Wildlife Refuge, in 1993.</b> (Note: row mean (O) that share the same capital letter are not significantly different)			
Analyte	Grasshoppers /Field Treatments (mg/kg dry weight)		ANOVA Results
	Fallow	Sorghum	[F(degrees freedom), P]
Al	119.29 A	27.11 B	F(1,4)=8.9, P=0.04
As	0.80 A	2.03 B	F(1,4)=13.8, P=0.02
B	26.5 A	21.3 A	F(1,4)=2.1, P=0.22
Ba	24.5 A	10.8 A	F(1,4)=6.8, P=0.06
Cd	0.3 A	0.2 A	F(1,4)=0.6, P=0.50
Cr	0.6 A	0.5 A	F(1,4)=1.1, P=0.35
Cu	64.1 A	64.4 A	F(1,4)=0.001, P=0.98
Fe	141.4 A	93.3 A	F(1,4)=2.9, P=0.17
Mg	1497.3 A	1135.6 A	F(1,4)=2.6, P=0.18
Mn	14.4 A	9.5 B	F(1,4)=8.8, P=0.04
Mo	0.7 A	3.2 B	F(1,4)=57.8, P=0.001
Ni	0.8 A	0.8 A	F(1,4)=0.03, P=0.87
Se	2.5 A	1.7 A	F(1,4)=3.0, P=0.16
Sr	75.8 A	36.5 A	F(1,4)=6.1, P=0.07
V	0.53 A	0.27 B	F(1,4)=2.8, P=0.17
Zn	133.3 A	128.7 A	F(1,4)=0.4, P=0.57

There were no statistically significant differences in boron, barium, cadmium, chromium, copper, iron, magnesium, nickel, selenium, strontium, and zinc concentrations detected in grasshoppers collected from the two cropping treatments. Grasshoppers collected from fallow fields contained statistically higher concentrations of aluminum, manganese, and vanadium than the sorghum fields. Whereas, grasshoppers collected from the sorghum fields contained statistically higher concentrations of arsenic and molybdenum.

Results of the metals analyses, in mg/kg wet weight for avian species collected in the vicinity of Pond No. 1 and Pond No. 4, are summarized in Table 16. Beryllium (detection limit = 0.02 mg/kg wet weight), cadmium (detection limit = 0.06 mg/kg wet weight), lead (detection limit = 0.50 mg/kg wet weight), and molybdenum (detection limit = 0.40 mg/kg wet weight) were below the analytical detection limits. With the exception of mercury detected in the red-winged blackbird sample, all other detected metals

were below levels of concern for predatory wildlife. The detected mercury concentration exceeded the avian predator protection limit 0.1 mg/kg wet weight, but was below the mammalian predator protection limit of 1.1 mg/kg (Eisler, 1987).

<b>Table 16. Metals Concentrations (in mg/kg wet weight) Detected in Avian Species Collected at Buffalo Lake National Wildlife Refuge in 1994</b> (Note: e is embryo; < is less than)				
Analyte	Pond No. 1			Pond No. 4
	Mourning Dove	Red-winged Blackbird	Mourning Dove-e	Unknown Species
Al	63.60	8.32	3.85	62.50
As	<0.01	<0.01	0.02	0.05
B	1.13	1.54	1.30	0.74
Ba	0.91	0.75	0.31	3.76
Cr	0.23	0.21	0.11	0.22
Cu	1.40	2.08	0.63	1.34
Fe	75.20	45.90	37.20	71.70
Hg	<0.01	0.17	<0.01	<0.01
Mg	289.00	226.00	100.00	282.00
Mn	2.80	1.12	0.54	1.62
Ni	<0.12	0.44	0.39	0.12
Se	0.27	0.51	<0.22	0.42
Sr	5.37	11.00	2.90	9.16
V	0.11	<0.05	<0.05	0.10
Zn	16.70	20.00	13.90	14.00

The mourning dove embryo sample was also analyzed in mg/kg wet weight for total-PCB content and organochlorine pesticide residues. The analytical detection limit for total-PCBs and the organochlorine compound, toxaphene was 0.24 mg/kg wet weight, while the analytical detection limit for the remaining 18 organochlorine compounds was 0.048 mg/kg wet weight. The red-winged blackbird egg samples were also analyzed for the same organochlorine constituents. In these samples the analytical detection limit for total-PCBs and toxaphene was 0.19 mg/kg wet weight, while the analytical detection limit for the remaining compounds was 0.048 mg/kg wet weight. None of the organochlorine compounds analyzed, including total-PCBs, were detected in concentrations above the respective analytical detection limits in any of the avian samples collected.

## CONCLUSIONS & RECOMMENDATIONS

In general, surface water in Tierra Blanca Creek appeared to be as contaminated in 1993 as it was in 1987. This may be attributed to residual nitrates and other nutrient compounds leaching from sediments which were previously saturated with contaminants because the rainfall event sampled was not of significant duration or intensity to cause the discharge of nutrient laden waste from cattle feedlots located upstream of the Refuge.

With the exception of Pond No. 2, surface water within the Refuge is relatively un-impacted by contaminants. Pond No. 2 contains elevated metals which may be attributed to the high clay content within the sediments. No obvious trends of contaminant infiltration into the groundwater were detected.

Farming of selected areas within the dry reservoir bed has been practiced at the Refuge since 1988. Measured soil phosphorus levels were lower in 1993 in comparison to the 1987 data; however, soil nitrogen levels were elevated in comparison to the 1987 data. Significant surface water inflow into the Refuge has not occurred since the Phase I study was conducted in 1987. Contaminants in run-off from CAFOs that can adversely effect an aquatic ecosystem may not represent concerns for farming or other management activities in grasslands. Nutrients that stimulated undesirable eutrophic conditions and caused fish kills in the reservoir now serve as fertilizer for crops in the dry reservoir bed. The nitrogen levels in the soils are elevated but do not appear to be causing nitrogen toxicosis to wildlife that feed on plants grown in these soils (Hickey, pers. comm., 1993). Metal concentrations detected in soils of the dry reservoir bed are not at levels considered detrimental to wildlife. Nitrogen levels detected in soils from the moist soil management units were more elevated than concentrations detected in the dry reservoir bed below Stewart Dike, but this is indicative that the moist soil management units are functioning in the capacity of wetlands and acting as sinks for nutrients carried into the Refuge via Tierra Blanca Creek. Total-PCBs and residual organochlorine pesticides do not appear to be a concern within the Refuge.

Based on the results of this study, vegetation and wildlife at the Refuge in their current state do not appear to be negatively impacted by nutrient overloading. As long as the dry reservoir bed within the Refuge is managed as a grass land, and not as a reservoir, there is little cause for concern. However, if the reservoir is allowed to fill again, eutrophication will likely occur and result in situations similar to the 1960s and 1970s fish kills. The moist soil management units serve as a limited buffer against contaminated stormwater intrusion from Tierra Blanca Creek. However, considering the large number of CAFOs permitted in the Tierra Blanca Creek watershed, it is recommended that additional moist soil management units be constructed to increase this buffering capacity. It is also suggested that regulatory agencies re-evaluate permitting so many large scale CAFOs in such a small watershed that contains sensitive habitats, because the system may not be able to dilute out the wastes in the event of a rainfall of significant intensity and duration and thus the potential exists that the Refuge could be adversely effected by millions of gallons of raw, untreated waste from these CAFOs.

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